Asian Journal of Chemistry Vol. 18, No. 4 (2006), 2662–2668

Synthesis and Characterization of Lanthanide(III) Complexes with 2,4-pyrimidine diamine-5-[(3,4,5-trimethoxy phenyl)methyl]

MANOHAR V. LOKHANDE
Department of Chemistry, Sathaye College, Mumbai-400 057 (India)
E-mail: lokhandemv2002@rediffmail.com

Complexes of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} with 2,4-pyrimidine diamine-5-[(3,4,5-trimethoxy phenyl)methyl] have been prepared. The structures of the complexes have been established on the basis of elemental analysis, magnetic moment, infrared, thermal analysis, X-ray powder diffraction and electronic spectra. The complexes are active towards gram-positive bacteria. The ligand is bonded through nitrogen and slight participation with 4*f* electron in bond formation..

Key Words: Lanthanide(III) complexes, 2,4-Pyrimidine diamine-5-[(3,4,5-trimethoxy phenyl)methyl].

INTRODUCTION

Compounds containing pyrimidine ring play a significant role in many biological systems[1]. The pyrimidine ring system present in nucleic acid, several vitamins and coenzymes etc. provides potential bonding sites for metal ions. Metal complexes of 2,4-pyrimidine diamine-5[(3,4,5-trimethoxy phenyl) methyl] with Cu^{2+}, Ni^{2+} and Co^{2+} have already been investigated[2], but no definite conclusion about their complexes with lanthanide metal ions has been reported.

In the present work, we report lanthanide(III) complexes with 2,4-pyrimidine diamine-5-[(3,4,5-trimethoxy phenyl)methyl] (Fig. 1).

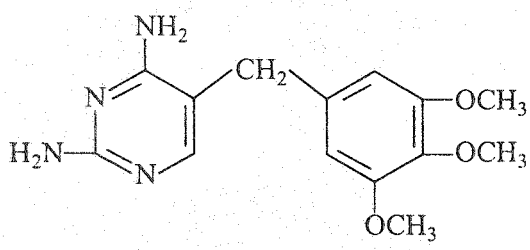

Fig. 1

EXPERIMENTAL

Lanthanide(III) chlorides were obtained form IREL (India) Mumbai and all reagents used in the present work were AR grade. Solvents were purified by known method. The ligand was obtained from Lupin Laboratories, Aurangabad. The elemental analyses were carried out using microanalyzer in Microanalytical

Laboratory at University Department of Chemistry at University of Mumbai, Mumbai. FTIR spectra were recorded by using KBr pellets on Perkin-Elmer Paragon-500 model FTIR spectrophotometer. Magnetic measurements were carried out on Gouy electro-balance using $Hg[Co(CNS)_4]$ as a calibrate. TGA and DTA were recorded at IICT Hyderabad using Toledo star© model thermal analyzer, using atmospheric nitrogen in the range 25–1000°C at the rate of 10°C/min. X-ray powder diffractions were recorded on Jeol-8030 double goniometry X-ray powder diffractometer at Tata Institute of Fundamental Research, Mumbai.

Preparation of complexes: The 0.25 molar solutions of metal chloride and ligand were prepared in ethanol. These solutions were mixed in 1 : 3 stiochiometric ratios and refluxed for *ca.* 3 h using water condenser at 80°C. The pH of the reaction mixture was adjusted in between 6.1–6.5 using 0.50 m alcoholic ammonia solution. After complete refluxing the solid product was obtained. This solid product was filtered, washed with ethanol and dried at 60°C.

RESULTS AND DISCUSSION

The analytical and physical data are listed in Table-1.The molar conductivity of the complexes shows electrolytic nature[3] in 0.001 M solution of dimethyl formamide. The molar conductivity data are given in Table-1. The chlorides were estimated by Mohr's method[4]. Metal contents were estimated by AAS method. The spectral data of the chelating agent indicate that bands of two —NH_2 groups are at 3315 and 3121 cm^{-1} respectively. The chelating agent forms complexes with lanthanide(III) metal ions. The bands in the region between 3336–3320 and 3168–3141 cm^{-1} may be assigned to primary amine group and the bands at 1450 and 1590 cm^{-1} are assigned to ν(C=C) and ν(C=N) and the skeleton frequencies[5] respectively. Their spectra do not show any stretching, bending and rocking of the —OCH_3 group. The strong frequencies at 1657–1590 cm^{-1} are due to —CN coupled with phenyl ring

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF LANTHANIDE(III) COMPLEXES

Complexes (Colour)	Yield (%)	(m.p.) (°)	% Analysis: Found (Calcd.)					Ω (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
			C	H	N	Cl	Ln		
$[La(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Colourless)	72.4	282–287	43.73 (43.53)	5.03 (4.96)	14.57 (14.42)	9.24 (9.09)	12.04 (11.96)	158.6	Diamag
$[Pr(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Light green)	74.5	288-292	43.69 (43.59)	5.02 (4.89)	14.56 (14.45)	9.23 (9.06)	12.20 (12.06)	162.4	3.55
$[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Lavender)	69.3	278-282	43.54 (43.45)	5.01 (4.92	14.51 (14.42)	9.20 (8.98)	12.44 (12.29)	156.2	3.66
$[Sm(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Tan)	62.8	273-277	43.33 (43.23)	4.98 (4.84)	14.44 (14.33)	9.15 (8.95)	12.90 (12.75)	157.3	2.13
$[Gd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Cream)	66.3	266-270	43.05 (42.99)	4.95 (4.82)	14.35 (14.25)	9.09 (8.88)	13.42 (13.28)	162.9	7.89
$[Tb(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Brown)	64.9	254-258	42.99 (42.84)	4.94 (4.83)	14.33 (14.22)	9.08 (8.91)	13.54 (13.43)	158.3	9.61
$[Dy(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ (Colourless)	64.5	263-267	42.86 (42.68)	4.92 (4.84)	14.28 (14.20)	9.05 (8.89)	13.80 (13.72)	163.9	10.46

vibration[6]. A comparison of the amino spectra shows that the strong band at 1657cm^{-1} with shoulder at 1670 cm^{-1} may be assigned to symmetric and asymmetric >C=N vibrations respectively. A close examination of the infrared spectral data reveals that both the amino groups of the ligand form a bridge between two amino groups with metal ions. Thus it may be concluded that the ligand form metal complexes with lanthanide(III) metal ions. Some changes were observed in >NH and > C=N vibration band, which indicates that the coordination occurs through these sites[7]. The coordination is through two amines of nitrogen with metal ions, but there is no indication about the nitrogen of the pyrimidine ring. In the far infrared region spectral data reveal bands at 532–515 and 456–433 cm^{-1} which may be assigned to (M—N) and (M—O) respectively[8]. The bands are observed in all complexes in the region between 3745–3736 and 3561–3528 cm^{-1} due to the coordination of two water molecules with the central metal ion.

The electronic spectra of Pr^{3+}, Nd^{3+} and Sm^{3+}complexes show bands at lower energies as compared to those in their aqua metal ions[9]. This may be attributed to the lowering of interelectronic repulsion parameter on complexation[10]. The spectral parameters are given in Table-2 by evaluating the absorption intensities from beneath the absorption curve by the literature procedure[11, 12]. The observed bands in the spectra of $[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ complex are much larger (1–2 times) than those reported for aqua ions[13]. These higher values suggest that there is lowering of the symmetry around the central metal ion[11, 14]. The hypersensitivity transitions $^4I_{9/2} \rightarrow {}^4G_{5/2} : G_{7/2}$ for $[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ complex. The hypersensitive bands of the $[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ complex resemble the eight-coordination number[11, 12] and suggest a coordination number eight around the central metal ion. The nephelauxetic ratio β and bonding parameter $b^{1/2}$ suggest that there is some participation of 4*f* electrons in the bonding. The positive values of Singh's parameter δ % which indicates a weak covalent interaction between the

TABLE-2
ELECTRONIC SPECTRAL VALUES AND ASSIGNMENTS

Complexes	Band (cm^{-1})	Assignments	pectral parameter
$[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$	11415	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	
	12438	$\rightarrow {}^4F_{5/2}$	$\beta = 0.995$
	13228	$\rightarrow {}^4F_{7/2}$	
	14451	$\rightarrow {}^4F_{9/2}$	$b^{1/2} = .00803$
	17065	$\rightarrow {}^4G_{5/2}$	
	18797	$\rightarrow {}^4G_{7/2}$	$\delta\% = 1.306$
	19084	$\rightarrow {}^4G_{9/2}$	
	22727	$\rightarrow {}^4P_{1/2}$	
$[Sm(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$	15822	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	$\beta = 0.98842$
	20491	$\rightarrow {}^4I_{11/2}$	$b^{1/2} = 0.0761$
	21367	$\rightarrow {}^4J_{13/2}$	$\delta\% = 1.77$
	22321	$\rightarrow {}^4G_{9/2}$	

metal ion and the ligand[14]. The correlation between the energy of some *J-J* transition and the M-L distance has been to estimate the coordination number of lanthanide (III) ion in the complex[15].

The La^{3+} complex is diamagnetic, while all other complexes are paramagnetic in nature. The room temperature magnetic moments (Table-1) deviate from Van Vleck[16, 17] values slightly. This indicates that only a little participation of *4f* electron in bonding in spite of being shielded by $5s^25p^6$ orbital. The $[Sm(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ complex exhibit slightly higher values for magnetic moments, which may be due to the thermal population of next higher j-j levels of metal ion arising from the first order Zeeman effect[18].

The intensities of diffracted X-ray as a function of Diffraction Angle θ for $[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ and $[Sm(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ 22 were recorded over the range 10–40. The interplanar spacing has been calculated from the position of intense peak using Bragg's relationship. The calculated spacing and parameters together with the relative intensities with respect to the most intense peak are given in Table-3 (A) and (B). These peaks are attributed to the diffraction of X-rays by planes of metal ions and are known as basal planes. The powder diffraction patterns were indexed on a monoclinic cell by using POWD In-and-Out program and Back Cal program on computer given by Ito[19]. The lattice parameters were refined by least squares method. The complexes were crystalline with monoclinic system having space group $C_{2/m}$ or $P_{2/m}$ containing Z = 6 formula factor[20–24]. The densities of the complexes were calculated by using toluene as solvent. The observed densities of the complexes were compared with calculated density.

TABLE-3A
X-RAY POWDER DIFFRACTION DATA FOR $[Pr(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ COMPLEX

a (Å) = 25.7160; b (Å) = 23.8225; c (Å) = 31.3155; D_{obs} = 1.8497; D_{cal} = 1.8554:
Space group = $C_{2/m}$ or $P_{2/m}$; α = 90°; β = 102.404°; γ = 90°; Z = 6;
crystal system = monoclinic; V $(Å)^3$ = 6213.39.

Sr. No.	2θ	h	k	*l*	d_{obs}	d_{cal}	I/I_0
1.	12.70	0	1	0	6.9701	6.9675	26
2.	13.89	0	1	1	6.1275	6.1312	55
3.	14.45	1	1	1	5.6230	6.6204	42
4.	15.65	1	1	2	4.3554	4.3520	43
5.	23.53	7	0	2	3.6685	3.6930	100
6.	25.08	3	1	2	3.5201	3.5201	35
7.	27.16	0	2	1	3.3624	3.3634	24
8.	27.68	2	2	0	3.3313	3.3318	20
9.	28.45	1	2	1	3.2678	3.2712	76
10.	32.06	1	0	4	3.0079	3.0083	25
11.	35.96	3	0	4	2.5754	2.5740	26
12.	39.12	0	3	1	2.2858	2.2858	21
13.	39.81	8	0	2	2.2540	2.2524	26

Thermogravematric analysis and differential thermal analysis results (Table-4) of some $[Ln(C_{14}H_{18}N_4O_3){\cdot}2H_2O]Cl_3$ complexes are reported. The study of $[Pr(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$, $[Nd(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$, $[Sm(C_{14}H_{18}N_4O_3)_3{\cdot}2H_2O]Cl_3$ indicates that the complex is stable at room temperature[25, 26] and

decomposes in three steps. The weight loss in the vicinity of 120–280°C suggests the volatization of two water molecules[27].

TABLE-3B

X-RAY POWDER DIFFRACTION DATA FOR $[Sm(C_{14}H_{18}N_4O_3)_3 \cdot 2H_2O]Cl_3$ COMPLEX

a (Å) = 17.7546; b (Å) = 10.4954; c (Å) = 18.7865; α = 90°; β = 114.948°; γ = 90°; D_{cal} = 1.9162; D_{obs} = 1.9134; Space group = $C_{2/m}$ or $P_{2/m}$; crystal system = monoclinic; V $(Å)^3$ = 6045.36; Z = 6

Sr.No.	2θ	h	k	*l*	d_{obs}	d_{cal}	I/I_0
1.	10.10	1	1	0	8.7577	8.7918	59
2.	10.46	2	0	0	8.0577	8.0489	60
3.	12.36	1	1	1	7.161	7.1684	66
4.	13.64	1	0	2	6.4918	6.4823	52
5.	14.04	2	0	1	6.3077	6.3201	60
6.	15.96	3	0	2	5.7685	5.768	100
7.	16.94	0	2	0	5.2338	5.2477	49
8.	24.18	2	1	3	3.6806	3.6763	36
9.	24.80	4	0	1	3.5901	3.5922	40
10.	26.00	0	3	1	3.327	3.4269	53
11.	26.22	4	1	1	3.3987	3.3987	58
12.	28.68	3	2	2	3.1125	3.1115	47
13.	33.10	4	2	2	2.7063	2.7071	27
14.	33.68	4	1	3	2.6843	2.6845	28
15.	34.32	2	3	3	2.6129	2.61196	40
16.	37.08	2	4	1	2.4245	2.4233	27
17.	37.82	2	3	4	2.3787	2.3776	21
18.	38.44	5	1	3	2.3418	2.3394	30

TABLE-4

THERMAL ANALYSIS [TGA/DTA] OF LANTHANIDE (III) COMPLEXES

Complexes	Peak range (°C)	Theo-retical (%)	Experi-mental (%)	Possible leaving group
$[Pr(C_{14}H_{18}N_4O_3)_3 \cdot 2H_2O]Cl_3$	110–280	18.98[a]	18.16	$2H_2O$, $3OCH_3$, C_6H_2, CH_2
	310–390	43.62[b]	44.43	C_6H_2, $3OCH_3$, $C_6H_2N_2$
	410–790	71.43[a]	71.99	Pr_2O_3
$[Nd(C_{14}H_{18}N_4O_3)_3 \cdot 2H_2O]Cl_3$	120–180	9.67[a]	9.142	H_2O, C_6H_2
	200–390	37.92[b]	38.15	$C_6H_2N_2$, $6OCH_3$, $2NH_2$, CH_2
	410–800	70.93[a]	71.48	Nd_2O_3
$[Sm(C_{14}H_{18}N_4O_3)_3 \cdot 2H_2O]Cl_3$	110–280	17.45[a]	17.28	$2H_2O$, $3OCH_3$, C_6H_2
	300–380	44.45[b]	44.35	$C_{12}H_4N_2$, $3OCH_3$, CH_2, $2NH_2$
	400–800	71.07[a]	72.89	Sm_2O_3

[a]Endothermic reaction, [b]Exothermic reaction.

The proposed structure of the complex is given in Fig. 2.

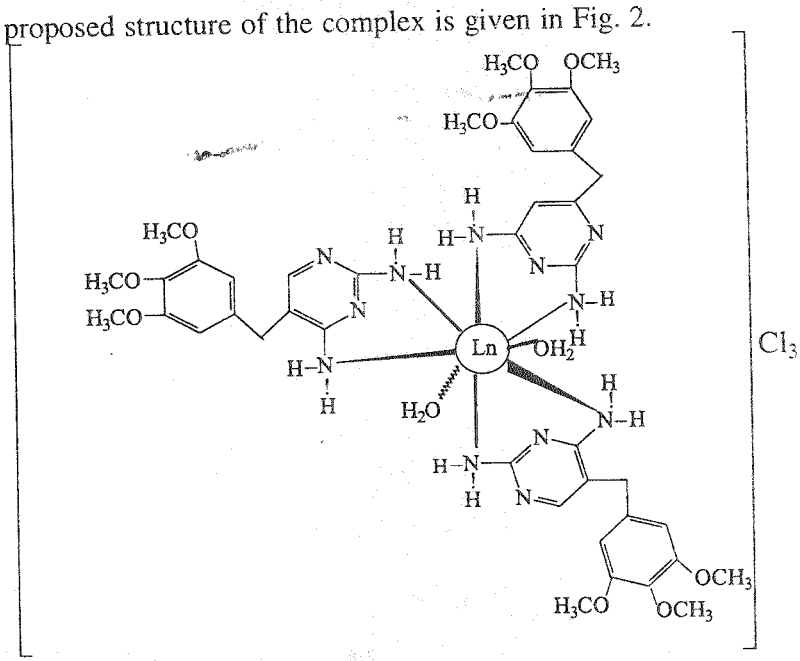

Fig. 2. Structure of the complex Ln^{3+} metal ions with 2,4-pyrimidine diamine-5[(3,4,5-trimethoxy phenyl)methyl].

The studies of antimicrobial activity indicate that amongst other factors, constitution of ligand, its coordination to the metal ion, the nature of metal ion in the complex and strain of the microorganism have important influence on antimicrobial activity. The 2,4-pyrimidine diamine-5-[(3,4,5-trimethoxy phenyl) methyl] and their complexes show that more activity toward *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus* and *Salmonella typhi* is more inhibition of growth towards Gram-positive bacteria.

ACKNOWLEDGEMENTS

The authors thank Dr. M.N. Deshpande, Dr. A.G. Kulkarni, E.M. Khillare, Dr. S.M. Maluste, Rajendra, Sou, Lalita M. Lokhande, Mayuri and Vishant for their cooperation and help in research work.

REFERENCES

1. N. Saha and S.K. Kar, *J. Inorg. Nucl. Chem.*, **39**, 195 (1977).
2. J.M. Tsangaris, D. Sotiropulos and A.G. Galinos, *Inorg. Nucl. Chem. Lett.*, **14**, 375 (1978).
3. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
4. A.I. Vogel, A Textbook of Qualitative Inorganic Analysis, 3rd Edn., Longman, London (1969).
5. B.E. Douglas, *Inorg. Synth.*, **18**, 2 (1978).
6. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley-Interscience, New York (1986).
7. C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, pp. 258–265 (1963).

8. N.C. Mishra, *J. Indian Chem.Soc.*, **55**, 839 (1978).
9. G.P. Choplin, D.E. Henrie and K. Buijs, *Inorg. Chem.*, **5**, 193 (1966).
10. C.E. Schaffer and C.K. Jorgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).
11. D.G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967).
12. ———, *Inorg. Chem.*, **7**, 473 (1968).
13. K. Iftikhar, *Inorg. Chim. Acta*, **129**, 261 (1987).
14. G. Marcotrigiiano and G.C. Pellacani, *Inorg. Nucl. Chem. Lett.*, **11**, 643 (1975).
15. S.P. Tandon and P.C. Mehta, *J. Chem. Phys.*, **52**, 4896 (1970).
16. K.B. Yatsimirski and N.K. Devidenko, *Coord. Chem. Rev.*, **27**, 223 (1979).
17. J.H.V. Vleck and A. Frank, *Phys. Rev.*, **32**, 1494 (1929).
18. T.J. Marks, *Prog. Inorg. Chem.*, **24**, 51 (1978).
19. T. Ito, X-ray Studies on Polymorphism, Maruzen Co. Ltd., p. 187 (1980).
20. JPDPDC, X-ray diffraction data, 40-1707 (1998).
21. M.A. Zoroddu, L. Naldini, N. Masciocchi and F. Demartin, *Inorg. Chim. Acta,* **128**, 179 (1987).
22. F. Demartin, M. Manassero, L. Naldini and M.A. Zoroddu, *Inorg. Chim. Acta*, **77**, L213 (1983).
23. L. Naldini, M.A. Cabros, M.A. Zoroddu, F. Demartin, M. Manassero and M. Sansoni, *Inorg. Chim. Acta.*, **88**, 45 (1984).
24. T.F. Koetzle and G.J.B. Williams, *J. Am. Chem. Soc.*, **98**, 2074 (1976).
25. R.K. Agarwal and S.K. Gupta, *Pol. J. Chem.*, **61**, 341 (1987).
26. M.S. Saamant, P.N. Namoodiri and S.R. Dharwadkar, *Mater. Chem. Phys.*, **35**, 120 (1993).
27. M. Shyamala, S.R. Dharwadkar, M.D. Karkhanavala and V.V. Deshpande, *Thermochim. Acta*, **44**, 249 (1981).

(*Received*: 11 July 2005; *Accepted*: 10 April 2006) AJC-4779