

Spectral Studies of Ln(III) Complexes with Pyridine Propanamine- γ -(4-chlorophenyl)-N,N-dimethyl-2-maleate

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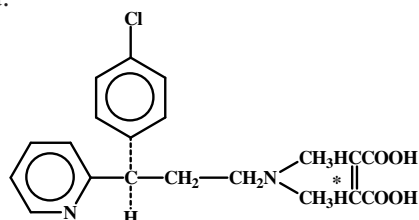
Complexes of La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} with pyridine propanamine- γ -(4-chlorophenyl)-N,N-dimethyl-2-maleate have been prepared, structures of the complexes have been established on the basis of elemental analysis, magnetic moment, infrared, thermal analysis, X-ray powder diffraction and electronic spectra. The ligand is bonded through nitrogen of propanamine and nitrogen of pyridine with metal ions. The magnetic moment studies indicate that, it is slightly participation with $4f$ electrons in bonding. The X-ray powder diffraction studies indicate that, the unit cell is monoclinic and space group of complexes is $C_{2/m}$ or $P_{c/m}$. This ligand is anti-histaminic and active towards gram positive and gram negative bacteria.

Key Words: Ln(III), Complexes, Pyridine propanamine- γ -(4-chlorophenyl)-N,N-dimethyl-2-maleate.

INTRODUCTION

There has been a growing interest in the coordination chemistry of lanthanides¹ due to their potential application as luminescent probes in medicine and biology² as contrast agents in magnetic resonance imaging³⁻⁶ and as mild reagents and catalysis in organic synthesis⁷. These applications require a precise knowledge of the coordination properties of lanthanide ions. Complexes containing macrocyclic hard donor ligand have been the most studied. This creates an interest in lanthanide complexes with γ (4-chlorophenyl)-N,N-dimethyl-2-pyridine propanamine maleate. This chelating agent contains nitrogen donor atoms from their potential application. It is dibasic organic compound containing two carboxylic groups and nitrogen of pyridine ring and nitrogen in chain.

Structure of ligand:



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This ligand is 99.2 % pure and its purity is checked on thin layer chromatography. We have initiated studies on the coordination chemistry of γ (4-chlorophenyl)-N,N-dimethyl-2-pyridine propanamine maleate with inner transition metal ions like La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} in an attempt to examine their mode of bonding.

EXPERIMENTAL

Preparation of complexes: The 0.2 molar of metal chloride and ligand solutions were prepared in ethyl alcohol. These solutions were mixed in 1:3 stoichiometric ratios; the solutions were slowly added with constant stirring to an acidic aqueous metal solution. The pH of the solution was adjusted to about 5.8 to 6.3 by adding 0.01 molar alcoholic ammonia solution. The resulting mixture was refluxed for 3 h in water bath, using water condenser. After three hours the precipitate was obtained. Then this precipitate was cooled, filtered, washed with ethyl alcohol and dried at 60 °C. These complexes were used for elemental analysis, IR, UV-Vis, X-ray powder diffraction, magnetic moment and thermal analysis.

The infrared spectra were recorded using KBr pallets on Perkin-Elmer Paragon-500 FTIR spectrophotometer and electronic spectra on Cintra-500 UV-Vis spectrophotometer at UDCT-Mumbai. Magnetic susceptibility measurements were carried out on Faraday electro-balance using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as calibrate at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. The thermal data were recorded in the range 25-1000 °C at 10 °C /min using Mettler Toledo star^c system at C-MET-Pune. X-ray powder data were recorded on Joel-8030 Goniometry, using CuK α radiation at TIFR-Mumbai. The indexing of X-ray powder line was done by Ito's methods.

RESULTS AND DISCUSSION

The analytical and physical data are given in Table-1. The metal contents were determined by AAS. The chlorides were estimated by Mohr's method⁸. Molar conductivity was determined in dimethyl formamide using 10⁻³ molar solutions of complexes. The molar conductivity of the complexes was 1:3 electrolytic in nature⁹, which implies that the three chloride anions are present outside the co-ordination sphere. The complexes were decompose in the range 311-326 °C. The melting point and decomposition point are taken in open capillary and are incorrect. The metal ligand ratio of the complexes is 1:3. The complexes were mostly insoluble in organic solvents like benzene, acetone, acetonitrile, ether and chloroform. But these complexes are soluble in dimethyl formamide and dimethyl sulfoxide.

Infrared spectra: The bands observed in the range 3016-2969 cm⁻¹ and 2940-2852 cm⁻¹ in the spectra of ligand is for pyridine nitrogen and benzene ring¹⁰. The band at 1210 cm⁻¹ is assigned to tertiary nitrogen of dimethyl moiety¹¹ in ligand and it is shifted to in the range 1140-1110 cm⁻¹ in La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} complexes. This suggests that the involvement of tertiary nitrogen in complexation. The bands due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ mixed stretching vibrations

TABLE-1
ANALYTICAL AND PHYSICAL DATA

Complex (colour)	m.p. (°C) (Yield, %)	Elemental analysis (%): Theor. (Exper.)					Λ_m (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} (BM)
		C	H	N	Cl	M		
[La(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Colourless)	315-318 (71.1)	53.0 (52.8)	5.42 (5.18)	7.72 (7.42)	19.60 (19.24)	12.77 (12.65)	169	Dimag
[Pr(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Greenish)	312-314 (75.5)	52.9 (52.34)	5.41 (5.22)	7.70 (7.46)	19.56 (19.32)	12.93 (12.68)	178	3.48
[Nd(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Violet)	304-307 (70.4)	52.74 (52.38)	5.39 (5.09)	7.69 (7.38)	19.50 (19.22)	13.69 (12.87)	158	3.52
[SmC ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Tan)	298-301 (73.8)	52.44 (52.18)	5.37 (5.04)	7.64 (7.35)	19.39 (19.14)	13.67 (13.46)	165	1.67
[Gd(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Cream)	291-294 (79.1)	52.12 (51.78)	5.33 (4.83)	7.60 (7.28)	19.27 (19.02)	14.21 (14.02)	168	7.96
[Tb(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Brownish)	275-278 (75.2)	52.04 (51.77)	5.32 (4.88)	7.58 (7.39)	19.24 (18.95)	14.34 (14.08)	175	9.75
[Dy(C ₁₆ H ₁₉ ClN ₂) ₃ ·H ₂ O]Cl ₃ (Colourless)	251-254 (78.5)	51.87 (51.42)	5.31 (4.82)	7.56 (7.36)	19.18 (18.86)	14.61 (14.39)	157	10.58

are found in the ligand at 1585 and 1550 cm⁻¹ and they were shifted at 1538-1524 cm⁻¹ and 1520-1510 cm⁻¹ in the complexes indicating that, involvement of nitrogen atom of pyridine ring in the complexation¹². The sharp band at 1701 cm⁻¹ in spectra of the ligand may be due to $\nu(\text{C}=\text{C})$ of maleate ion and this band is not observed in the complexes. It was reported¹³ that some bands observed in the region 1160-1060 cm⁻¹ are due to pyridine vibration. In the present case similar bands were observed in the ligand and the complexes but they were of quite weak intensity. New bands are observed at 3510-3480 cm⁻¹ in the spectra of complexes which correspond to involvement of one water molecule in the co-ordination sphere. The new bands are observed near 495-475 cm⁻¹ in the infrared spectra of complexes may be assigned to $\nu(\text{M}-\text{N})$ ¹³ assigned to coordinated nitrogen atom of pyridine ring and the bands at 460-440 cm⁻¹ assigned to $\nu(\text{M}-\text{O})$ ¹⁴.

Electronic spectra: The electronic spectra of [Pr(C₁₆H₁₉ClN₂)₃·H₂O]Cl₃ and [Nd(C₁₆H₁₉ClN₂)₃·H₂O]Cl₃ complexes were recorded in dimethyl formamide. The spectral data along with the various calculated bonding parameters are included in Table-2. All the bands showed a weak perturbation due to complex formation and an increase in intensity compared to the aquo ion¹⁵, presumably due to nephelauxetic effect. The absorption band associated with nearly degenerate $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}; \text{G}_{7/2}$ of the [Nd(C₁₆H₁₉ClN₂)₃·H₂O]Cl₃ is known to exhibit strong hypersensitive behaviour¹⁶ making it especially suitable for probing the coordination number around the Nd³⁺ ion. The hypersensitive band profiles of the Nd³⁺ complex in solution states resemble those of the coordinated complex¹⁷. The spectral features in the hypersensitive band region of the present [Nd(C₁₆H₁₉ClN₂)₃·H₂O]Cl₃ complex were found to be identical in liquid states suggesting a similar environment around the metal ion. Various bonding

TABLE-2
ELECTRONIC SPECTRAL VALUES AND THEIR ASSIGNMENTS
Complexes-1: [Pr(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃; Complex-2: [Nd(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃
Wavelength: 380-900 nm

Complex No.	Band (cm ⁻¹)	Assignment	Spectral parameter
1	16892	³ H ₄ → ¹ D ₂	β = 0.9754
	20661	→ ³ P ₀	b ^{1/2} = 0.1109
	21367	→ ³ P ₁	δ % = 2.5220
	22522	→ ³ P ₂	η = 0.0125
2	11494	⁴ I _{9/2} → ⁴ F _{3/2}	β = 0.9698 b ^{1/2} = 0.1228 δ % = 3.1140 η = 0.0155
	12500	→ ⁴ F _{5/2}	
	12821	→ ⁴ F _{7/2}	
	15773	→ ² F _{9/2}	
	17241	→ ⁴ G _{5/2}	
	19084	→ ⁴ G _{7/2}	
	19608	→ ⁴ G _{9/2}	
	24272	→ ² P _{1/2}	

parameters like nephelauxetic ratio (β), bonding parameter (b^{1/2}), η and Sinha's parameter (δ %)¹⁸ for the complexes. All these parameters suggest a weak covalent bonding between the metal and ligand and co-ordination number is seven. Electronic spectra of [Nd(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃ complex.

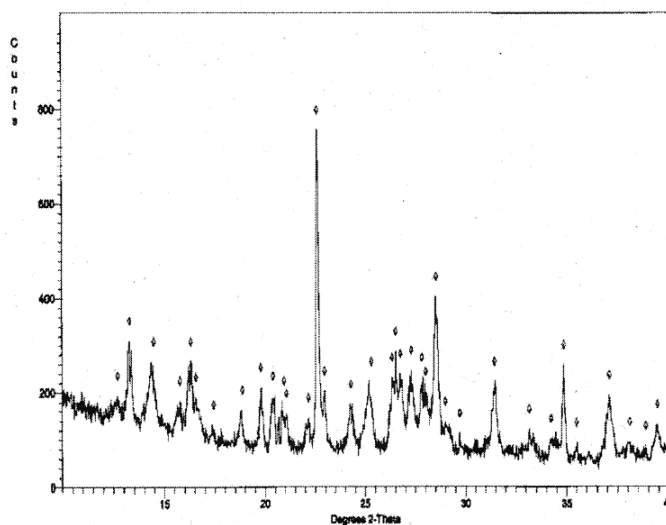
Magnetic moment: The magnetic moment values of the lanthanide(III) complexes at room temperature are found to be closed, to the value calculated using the formula¹⁹.

$$\mu = g\sqrt{J(J+1)}$$

The 4*f* electrons of lanthanide remain invariant to the coordination environment, as the 4*f*-orbital are deeper inside the closed shell. The *para* magnetism is only due to the presence of unpaired electrons like Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, Tb³⁺ and Dy³⁺ metal ions. There is no exchange interaction, as La³⁺ possesses no unpaired electron, hence it is diamagnetic. The complexes show a little deviation from Van Vleck values²⁰ and indicate participation of 4*f* electrons in bonding. The slightly higher value of magnetic moments in case of the samarium complex is due to temperature dependent magnetism because of low *J-J* separation²¹.

X-ray powder diffraction: The X-ray powder diffraction of [Pr(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃ and [Tb(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃ complexes indicate high crystallinity of these complexes. The major reflexes were measured and corresponding 'd' values were obtained by Bragg's equation (nλ = 2d sin θ). The indexing of major reflexes were carried out using least square method and miller indices h, k, l were calculated and refined by using various program on computer like Back-cal, powdin and cerelef^{22,23}. The complexes are monoclinic crystal system with formula factor Z = 8. The lattice parameters along with dobs and dcal values are summarized in Table-3. The correctness of these values was confirmed by matching with the observed density for [Pr(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃ complex 1.4803 cm³ and [Tb(C₁₆H₁₉CIN₂)₃·H₂O]Cl₃

complex 1.4389 g/cm^3 . The unit cell is monoclinic and space group of complexes is $C_{2/m}$ or $P_{c/m}^{24}$.



X-Ray powder of $[\text{Pr}(\text{C}_{16}\text{H}_{19}\text{ClN}_2)_3 \cdot \text{H}_2\text{O}]\text{Cl}_3$ complex

TABLE-3
X-RAY POWDER DIFFRACTION DATA FOR $[\text{Pr}(\text{C}_{16}\text{H}_{19}\text{ClN}_2)_3 \cdot \text{H}_2\text{O}]\text{Cl}_3$ COMPLEX
a (Å) = 24.0403; b (Å) = 8.8433; c (Å) = 14.7038; $\alpha = 90^\circ$; $\beta = 95.193^\circ$; $\gamma = 90^\circ$
 $D_{\text{cal}}(\text{g/cm}^3) = 1.5033$; $D_{\text{obs}}(\text{g/cm}^3) = 1.4803$; Space group = $C_{2/m}$ or $P_{2/m}$;
Crystal system = Monoclinic; $V(\text{Å})^3 = 7432.80$; Z = 8

Sr. No.	h	k	l	D_{obs}	D_{cal}	I/I_0
1	0	1	0	8.8451	8.8433	68
2	0	1	1	7.5634	7.5700	100
3	3	0	1	6.7479	6.7553	59
4	3	1	0	5.9376	5.9247	45
5	2	1	2	4.9718	4.9700	31
6	0	2	0	4.4176	4.4217	30
7	0	2	1	4.2382	4.2329	32
8	6	0	0	3.3391	3.9903	27
9	3	1	3	3.6479	3.6489	36
10	5	1	2	3.5339	3.5307	28
11	0	3	0	2.9478	2.9478	20
12	2	3	1	2.7968	2.7967	25
13	9	0	1	2.5765	2.5767	18
14	10	1	0	2.3094	2.3110	18

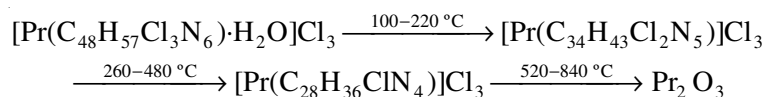
Thermal analysis: The thermogravimetric and differential thermal analysis of $[\text{Pr}(\text{C}_{16}\text{H}_{19}\text{ClN}_2)_3 \cdot \text{H}_2\text{O}]\text{Cl}_3$ complex were studied²⁵. These complexes are stable at room temperature. The thermal loss is due to exo and endothermic process^{26,27}.

[Pr(C₁₆H₁₉ClN₂)₃·H₂O]Cl₃ complex: The thermogravimetric and differential thermal analysis of praseodymium complex of pyridine propanamine-γ-(4-chlorophenyl)-N,N-dimethyl indicates that, the complex is stable at room temperature and shows two endothermic peak and one exothermic peak.

In the temperature range 100-220 °C, there is loss of one water molecule, which is present inside the coordination sphere of the complex and some organic part of complex. The experimental percentage loss is calculated from thermogravimetric curve is 22.47 which is comparable with theoretical percentage loss. The differential thermal analysis peak is endothermic. The presence of coordinated water molecule is confirmed from infrared spectra. The possible leaving groups are H₂O, C₅H₅N, C₆H₄Cl, C₃H₅.

In the temperature range 260-480 °C some organic part of complex is lost. The experimental percentage loss is 40.58 and theoretical percentage loss is 40.41. The differential thermal analysis peak is exothermic. The possible leaving groups are and C₅H₅N, C₆H₄Cl.

In the final stage, in the temperature range 520-840 °C complex is decomposed and converts into praseodymium oxide (Pr₂O₃). The experimental percentage loss is calculated from thermogravimetric curve is 69.54 and is comparable with theoretical percentage loss is 69.67. The probable scheme of decomposition of the complex is postulated as:



ACKNOWLEDGEMENTS

The authors thanks UGC for providing financial support, TIFR-Mumbai, IIT-Mumbai, Ajay Patil, R.V. Lokhande, E.M. Khillare, Pratap Dhabale Lalita, Mayuri and Vishant for their co-operation and help in research work.

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(Received: 16 January 2009;

Accepted: 9 September 2009)

AJC-7848

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