
Synthesis and Spectral Characterization of Ln(III) (Ln=La ,Pr, Nd, Sm, Gd, Tb and Dy) Complexes Of Schiff Base Derived From 4-Aminoantipyrine And 4-Methylcinnamaldehyde

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Abstract

Schiff base ligand **L** was synthesized by the general condensation of 4-aminoantipyrine and 4-methylcinnamaldehyde. The synthesized Schiff base was used for complexation with Ln(III) nitrate salt (La = La, Pr, Nd, Sm, Gd, Tb and Dy) to form complex of the general formula $M(NO_3)_2L_2$. The synthesized complexes were characterized using elemental analysis, ¹H NMR, IR, UV-Vis and TGA. The characterization data reveal that the Schiff base behaves as neutral bidentate and coordinated through azomethine nitrogen and carbonyl oxygen. IR data confirms that nitrate binds in a bidentate fashion. The molar conductance data show that the complexes are non ionic in nature with all three nitrate inside the coordination sphere. Thus lanthanide ions are surrounded by eight oxygen atom and two nitrogen atom and hence lanthanide ion show a coordination number of 10 in the synthesized complexes.

Keywords: Schiff Base, Lanthanide Complexes, IR, UV-Vis, TGA

1. INTRODUCTION

Schiff bases are very useful ligands in the synthesis of Lanthanide metal complexes. Symmetric and asymmetric Schiff base ligands can provide suitable donor sets capable of holding three metal ions in a linear complex. In particular, an asymmetry in the donor groups of the ligand can be exploited to obtain heterometallic linear complexes with some control over the position of the metals [1]. Schiff bases are prepared by condensation of an aldehyde or ketone and an amine. This simple reaction can be exploited with di-amines to obtain multiple coordination pockets in one ligand. Furthermore, the organic groups that form the aldehyde and amine can be varied practically at one's will to provide further functionality to the final ligand. Most often in coordination chemistry the aldehyde is salicylaldehyde. The versatility of these ligands that can be coordinated to lanthanides makes them very widely used to obtain coordination complexes with applications in materials science [2], magnetic materials [3–5] or catalysis [6].

The effective use of lanthanide(III) complexes, depends much upon their donor environments, structural geometries and thermodynamic stabilities. Because of effective shielding of 4f orbitals in trivalent lanthanides ($4f^n 5s^2 5p^6$), the crystal field effect and directional influence of the metal ions are weak. The small difference in property that occurs across the series is governed by their ionic radii, which decrease monotonically with the increase of atomic number.

In the last decades lanthanide complexes have attracted much attention not only for being valuable catalysts in organic synthesis but also for their wide applications in material and biological sciences mainly due to their very narrow emission bands, long excited-state lifetimes and large Stokes shifts, etc. They can be used in the design of novel luminescent probes in biomedical assays, fluorescent lighting, luminescence sensors,

electroluminescent devices and UV dosimeters [7 – 9]. The luminescent intensity of lanthanide complexes is strongly dependent on the efficiency of organic ligand to absorb light, the efficiency of energy transfer, and the efficiency of lanthanide metal luminescence. Significant efforts have already been made to design and synthesis ligands having selective ability to coordinate lanthanide ions, protect them from deactivation due to interaction with solvent molecules, and enhanced their luminescence by providing proper conjugate absorption groups suitable for energy transfer [10,11].

Prompted by these applications, in this work, bidentate Schiff base ligand **L** (4-[(N-4-MethylCinnamalidene)Amino]-Antipyrine) and its lanthanide(III) nitrate (La, Pr, Nd, Sm, Gd, Tb and Dy) complexes were prepared and characterized by elemental analysis, spectral analysis (Mass, FT-IR, UV-vis), molar conductivity measurements, and thermogravimetric studies.

2. EXPERIMENTAL

2.1. Material and Methods

All the chemicals were used of Anala R grade and received from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

2.2 General procedure for the synthesis of Ligand (L)

A solution of 4-methylcinnamaldehyde (1mmole, 0.146 g) in absolute ethanol (30ml) was mixed with 4-aminoantipyrine (1.1mmole, 0.223g) in the same solvent. The reaction mixture was stirred for 1 h and then refluxed for 2-3 h on water bath. The progress of the reaction was monitored by TLC and after completion of the reaction the reaction mixture was left overnight. A yellow crystalline product was separated out, which was filtered off and recrystallized in the ethanol (yield 90%). The Scheme for the synthesis of Schiff base is given in **Figure 1**.

2.3 General procedure for the synthesis of metal complexes 1–7

Complex **1** was prepared by mixing a solution of lanthanum(III) nitrate (1 mmol) and 4[N-4 Methylcinnamalidene)amino]antipyrine (**L**) (2.1 mmol) in hot methanol (20 mL each). The reaction mixture was refluxed on water bath for 1h and then cooled at room temperature. The solid complex separated out which was washed with hot diethyl-ether. and dried under reduced pressure over P₄O₁₀. In a similar way the metal complexes **2–7** were synthesized. The Scheme for the synthesis of metal complexes is given in Figure 1 and their physical and analytical data is given in **Table 1**.

2.4 Analysis

IR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr disc. UV spectra were recorded in DMSO on UV-VIS-NIR Varian Cary-5000 spectrometer. Elemental analysis was carried out on Perkin Elmer 2400. TG analysis of samples was carried out using SDT-Q600 simultaneous TGA/DSC instrument at a heating rate of 8°C min⁻¹. Magnetic moment at room temperature of the complexes were calculated by Gouy's method, using Hg[Co(SCN)₄] as the calibrant. Molar conductance measurements of a 10⁻³ M solution of metal complexes in DMF were measured using a model-306 Systronics conductivity

3 Result and discussion

Schiff base **L** was prepared by mixing an equimolar amount of 4-methylcinnamaldehyde and 4-aminoantipyrine in absolute ethanol as shown in Figure 1.

Figure 1: Scheme for the synthesis of the Schiff base and Lanthanide complexes

The crystalline solid so obtained have different shades of Yellow due to the presence of chromophoric group (HC=N) in the molecule. All the lanthanide complexes are prepared by the direct reaction of Schiff base and corresponding lanthanum salt. All these complexes are crystalline solids, stable in air at room temperature and the melting points of the metal complexes are much higher than that of the ligands, which indicates that these complexes are much more stable as compared to the ligands. The complexes in 10^{-3} M DMF solution have low molar conductance value ($3.8 - 4.2 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating their non-electrolyte nature [12].

No.	Molecular formula	Ω_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Yield (%)	Elemental Analysis (%) found (calc.)			
				C	H	N	M ^a
L	$\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}$	-	90	76.01 (76.11)	6.32 (6.39)	12.61 (12.68)	-
1	$\text{La}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	4.1	60	50.94 (51.06)	4.15 (4.25)	12.62 (12.76)	13.98 (14.07)
2	$\text{Pr}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	5.2	58	50.86 (50.96)	4.14 (4.24)	12.60 (12.74)	14.10 (14.21)
3	$\text{Nd}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	3.8	65	50.66 (50.79)	4.15 (4.23)	12.53 (12.69)	14.40 (14.53)
4	$\text{Sm}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	4.20	72	50.35 (50.48)	4.10 (4.20)	12.50 (12.62)	15.02 (15.15)
5	$\text{Gd}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	3.98	53	50.00 (50.13)	4.02 (4.07)	12.40 (12.53)	15.50 (15.64)
6	$\text{Tb}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	3.36	58	49.96 (50.05)	4.03 (4.17)	12.40 (12.58)	15.65 (15.78)
7	$\text{Dy}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	3.80	62	49.75 (49.87)	4.01 (4.15)	12.32 (12.46)	15.90 (16.08)

M^a=La, Pr, Nd, Sm, Gd, Tb, Dy

3.1 ¹H NMR

The ¹H NMR spectra of the ligand was recorded in DMSO. The presence of azomethine proton of the aldimines was confirmed by observing one proton singlet at δ 8.9 ppm. Two doublets corresponding to one proton each assigned to CH=CH of was observed at δ 6.92 and 7.11 ppm, respectively. Signals due to

aromatic protons were observed at δ 7.31–7.72 ppm, while the aliphatic protons resonate in region of 2.42–3.56 ppm. All the protons are found in their expected region.

3.2 IR spectra

The IR spectra of Metal complexes is compared with IR spectra of ligand (L), there are certain shifts in the bands. Ligand (L) exhibits stretching of (C=N) stretching at 1600 cm^{-1} which on complexation shifted to lower wave number at $1530\text{--}1580\text{ cm}^{-1}$ suggesting that azomethine nitrogen are involved in coordination [13]. Similarly, C=O stretching vibration which appears at 1660 cm^{-1} in ligand L shifts to lower side $1610\text{--}1640\text{ cm}^{-1}$, which indicates the carbonyl oxygen in complex formation. A nitrate ligand can coordinate to the metal ion in three types, as monodentate, bidentate ligand, or uncoordinated ion [14–19]. For Ln(III) complexes, the separation ($\nu_4\text{--}\nu_1$) is approximately $150\text{--}165\text{ cm}^{-1}$, so in these complexes the nitrate group coordinated as bidentate ligand [20–21]. The presence of nitrate as counter ion was indicated from the IR spectra of L and 1:2 (M:L) complexes. These complexes show a band at $1384\text{--}1387\text{ cm}^{-1}$ [45–47]. The appearance of new bands in the spectra of metal ion complex at $420\text{--}440\text{ cm}^{-1}$ was due to (M-O) bond, while the band corresponding to M-N appear at $370\text{--}390\text{ cm}^{-1}$ in metal complexes 1-7 [23]. Thus the ligand L exhibits neutral bidentate behaviour and coordinates to the metal ion through azomethine nitrogen and carbonyl oxygen for La(III), Pr (III), Nd(III), Gd(III) Tb(III), Sm(III) and Dy(III) complexes. IR spectral data also reveal that NO_3^{-1} binds to Ln(III) complexes in a bidentate fashion. The IR spectral peaks of the ligand and the metal complexes 1 – 7 are given in Table 2.

3.3 Electronic Spectra

The UV–Vis absorption spectra of the Schiff base ligand [L] and its Ln(III) complexes were carried out in DMF at room temperature. The values of the absorption wavelength and its band assignments are listed in Table 3. The absorption of the ligand [L] is characterized by three main absorption bands at 244, 265 and 381 nm. The band appearing at lower energy is attributed to $n \rightarrow \pi^*$ transition of conjugation between the lone pair of electrons of p orbital of N atom in azomethine group and conjugated p bond of the benzene ring [24]. The bands appearing at higher energy are attributed to $\pi \rightarrow \pi^*$ of the benzene ring and $\pi \rightarrow \pi^*$ transition of the azomethine group [25,26]. The UV–Vis absorption spectra of all the Ln(III) Schiff base complexes show

Table 2 Infrared absorption frequencies (cm^{-1}) of lanthanide (III) nitrate complexes of L (4[N-4-methyl cinnamalidene)amino]antipyrine)

Assignments	→					→		
L	L	1	2	3	4	5	6	7
C-H, C=C, C-N	3090w	3005w	3030w	3060w	3060w	3055w	3050w	3055w
Stretchings	3060sh	2995w	2980w	2990sh	2985w	2980w	2990w	2990sh
	3045vw	2960w	2965w	2980w	2960w	2965w	2980w	2980w
	3010vw	2910w	2910w	2960w	2910w	2850w	2960w	2960w
	2975vw	2850w	2850w	2850w	--	2800w	2910w	2920w
(C=O) stretching	1660vs	1630s	1640s	1620s	1625s	1605s	1635sh	1610sh
pyrazolone	1600s	1600s	1600s	1595vs, br	1595s	1590vs, br	1590s	
(C=N) stretching	1600sh	1560m	1575s	1580m	1550sh	1570sh	1550w	1530w
(azomethine)	1580s	1570s	1540s	1530m	--	1530m	--	--
Ring stretching	1555sh	1525m ^a	1535m	1525m ^a	1500sh ^a	1490s,br ^a	1510m ^a	1510sh
Of 5-membered	1510s	1510s ^a	1515m ^a	1510s ^a	1500m,br ^a	1440sh	1490m,	1485s
Ring	1500s	1470s	1475w	1470s	1465w		1450w	1420sh
	1470m	1450w	1460vw	1460s	1450w		1430w	
CH ₃ -deformation	1430m	1415w	1415w	1410w	1420w	-	1400w	-
			1400m		1400w			

Table 2 Infrared absorption frequencies (cm⁻¹) of lanthanide (III) nitrate complexes of L (4[N-4-methyl cinnamalidene)amino]antipyrine)

Assignments	1	2	3	4	5	6	7	8	9
Ring stretching	1378w	1380w	1385w	1385s	1385s	1360vs	1380vs	1380vs	1380vs
		1360sh	1330s	1360vs	1325w			1335vw	1305sh
		1325m							
		1310sh							
N-phenyl	1270w	1310w	1300w	1310w	1320m	1290s,br ^a	1290s ^a	1290s ^a	1290s ^a
Stretching	1190vw	1290m ^a	1285m ^a	1290m ^a	1280w,br	1220w	1235w	1235w	1235w
		1240s	1240s ^a	1240s	1230m ^a	1175m.br	1180sh	1170s	1170s
		1200sh	1160m	1200sh	1175w				
		1170m	1170m						
In plane bending	1150s	1135m	1120m	1135m	1140sh	---	1130m	1125w	1125w
Of CH-N-CH ₃	1115sh				1110m				
Stretching									
CH ₃ -rocking	1090w	1070w	1070w	1070w	1040sh	1070w	1060w	1060w	1060w
	1065m	1050sh	1055w	1060sh					
	1035w								
Ring breathing	1020vw	1020m ^a	1020m ^a	1020m ^a	1020w ^a	1020m ^a	1025m ^a	1025m ^a	1025m ^a
Of benzene	990s			1000w	990vw				

a- coupled with nitrate absorptions.

similarities, which indicates similarity in their structures and generally show the characteristic bands of the free ligands with some changes both in frequencies and intensities. Upon complexation, the absorption bands of the complexes are slightly shifted to shorter wavelength (blue shift) compared to those of the free ligand. These modifications of the shifts and intensity of the absorption bands indicate the coordination of the ligand to the metal ion. In general, the lanthanide ions do not appreciably contribute to the spectra of their complexes, since f-f transitions are Laporte-forbidden and very weak in nature [27].

Table 3: λ_{\max} (nm) value of ligand L and metal complexes 1 – 7

No.	Compound	λ_{\max} (nm)	Band Assignment
L	C ₂₁ H ₂₁ N ₃ O	244, 265, 381	n → π π → π*
1	La(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	224, 249, 328	n → π π → π*
2	Pr(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	220, 244, 321	n → π π → π*
3	Nd(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	227, 248, 323	n → π π → π*
4	Sm(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	219, 250, 340	n → π π → π*
5	Gd(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	223, 255, 338	n → π π → π*
6	Tb(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	225, 259, 344	n → π π → π*
7	Dy(NO ₃) ₃ (C ₂₁ H ₂₁ N ₃ O) ₂	221, 260, 326	n → π π → π*

3.4 Thermal Studies

The TGA study of the synthesized metal complexes was studied under nitrogen atmosphere at $10^{\circ}\text{C min}^{-1}$, and the weight loss was measured from the ambient temperature up to 1000°C . The residues are rare earth oxides. The experimentally found and calculated weight losses are listed in **Table 4**. All the complexes show three steps decomposition leaving metal oxide as residue. The first step in the range of $120\text{--}245^{\circ}\text{C}$ initial weight loss corresponds to the loss of the coordinated nitrate group and some organic fragments. The second step in the temperature range $245\text{--}475^{\circ}\text{C}$ is due to loss of organic moiety. In the final step in range of $475\text{--}800^{\circ}\text{C}$, the remaining fragment lost out leaving metal oxide as the residue.

Table 4 : Thermal analysis data of metal complex 1- 7

Comp. No	Molecular Formula	Stages	Temp ($^{\circ}\text{C}$)	Residual Species	Mass Loss (%)			
					Found	Calc.		
1	$\text{La}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	120–245	La_2O_3	20.24	33.03		
		2 nd	245–465		21.28			
		3 rd	465–790		25.50			
2	$\text{Pr}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	125–235		Pr_2O_3		21.23	33.43
		2 nd	235–460				20.40	
		3 rd	460–810				25.19	
3	$\text{Nd}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	120–245	Nd_2O_3		24.12	33.46	
		2 nd	245–455			19.76		
		3 rd	455–700			22.93		
4	$\text{Sm}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	130–240		Sm_2O_3	21.45		36.74
		2 nd	240 – 475			16.34		
		3 rd	475 – 760			25.67		
5	$\text{Gd}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	120–245	Gd_2O_3		22.87	36.21	
		2 nd	245–475			19.4		
		3 rd	475–800			21.72		
6	$\text{Tb}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	120–230		Tb_2O_3	21.98		36.38
		2 nd	230–460			16.76		
		3 rd	460–780			25.27		
7	$\text{Dy}(\text{NO}_3)_3(\text{C}_{21}\text{H}_{21}\text{N}_3\text{O})_2$	1 st	125–235	Dy_2O_3		22.67	37.22	
		2 nd	235–465			19.23		
		3 rd	465–800			20.97		

Based on the characterization data it may be conclude that the ligand L behaves as neutral bidentate and coordinates with Ln(III) ion through azomethine nitrogen and oxygen. The nitrate ions binds bidentately, thus

the Ln(III) ion show a coordination number of 10 in the synthesized complexes. Based on above results following structure can be proposed for the synthesized complexes (**Figure 2**).

Figure 2: Proposed structure of metal complexes

4. Conclusion

In this paper we report the synthesis and characterization of Ln(III) (Ln = La, Pr, Nd, Sm, Gd, Tb and Dy) complexes of the Schiff base which prepared by condensation reaction of 4-aminoantipyrine and 4-methylcinnamaldehyde. The synthesized ligand and complexes was thoroughly elucidated by using various analytical and spectroscopic techniques like elemental analysis, ¹H NMR, IR, UV-Vis and TGA. The molar conductance value of metal complexes show their non-electrolytic nature. The complexes were found to be stable at room temperature. On the basis of the spectroscopic data it was concluded that Ln(III) coordinates to 8 oxygen atom (6 from nitrate and two from pyrazolone ligand) and two azomethine nitrogen and form a 10 coordinated metal complexes.

5 References

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