

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF Ln(III) (Ln=La ,Pr, Nd, Sm, Gd, Tb and Dy) COMPLEXES OF SCHIFF BASE DERIVED FROM ISONICOTINOMIDE AND 4-METHYLCINNAMALDEHYDE

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Abstract-Schiff base ligand L was synthesized by the general condensation of isonicotinomide 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(NO₃)₂L₂. 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. The coordination chemistry of lanthanide (III) ions is rapidly increasing, owing to the relevance of these compounds in basic and applied research in different scientific areas ranging from chemistry to material science to the life science [1–8]. Lanthanide coordination compounds are the subject of intense research efforts owing to their unique structures and their potential applications in advanced materials such as Ln-doped semiconductors [9], magnetic [10, 11], catalytic [12], fluorescent [13, 14], and nonlinear optical materials [15, 16]. It has been shown that ligands containing both nitrogen and oxygen donor atoms are good building blocks for the formation of various lanthanide coordination compounds [17–24]. Schiff bases continue to occupy an important position as ligands in metal coordination chemistry [25], even almost a century since their discovery. Schiff base metal complexes have played a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [26]. The lanthanide cations can promote Schiff base condensation and can give access to complexes of otherwise inaccessible ligands.

The stability of Lanthanide metal complexes depends upon number of factors, including the number and types of donor atoms present in the ligand and their relative positions with the Lanthanide metal complexes skeleton, as well as the number and size of the chelate rings formed on complexation[27]

On the other hand, the lanthanide complexes, involving the Schiff bases formed by the condensation of 2-acetylfuran and 4-aminoantipyrine, are not so common. Due to their special electronic configuration, lanthanide complexes have inspired many efforts on the design and synthesis as potential anticancer and antibacterial agents. Polydentate ligands such as Schiff bases, assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possess binding sites and cavities for various cations, anions, and organic molecules.

Prompted by these applications, in this work, bidentate Schiff base ligand L INH-MSAL[N-isonicotinamido 4-Methyl salicylaldimine and its lanthanide(III) nitrate (La ,Pr, Nd, Sm, Gd, Tb and Dy) complexes were prepared and characterized by elemental analysis, spectral analysis (¹H NMR 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 Isoniazid (1.1 mmole) in absolute ethanol (30ml) was mixed with 4-methyl salicylaldehyde (1 mmole) in the same solvent. The reaction mixture was stirred for 1 h and then refluxed for 5 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 85%).

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 (L) [N-isonicotinamido 4-Methyl salicylaldimine (2.1 mmol) in hot methanol (30 mL each). The reaction mixture was refluxed on water bath for 4h and then cooled at room temperature. The solid complex separated out which was washed with hot diethyl-ether. and dried under reduced pressure over P_4O_{10} . 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 $8^{\circ}\text{C min}^{-1}$. Magnetic moment at room temperature of the complexes were calculated by Gouy's method, using $\text{Hg}[\text{Co}(\text{SCN})_4]$ 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 2-acetylfuran and 4-aminoantipyrine in absolute ethanol. The lanthanide complexes are prepared by the reaction of synthesized Schiff base with corresponding lanthanum salt using methanol as solvent. The synthesized 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. Molar conductance value of the complexes **1–7** are in the range of $5.35 - 6.32 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, which indicates their non electrolytic behavior [28].

3.1 $^1\text{H NMR}$

The $^1\text{H NMR}$ spectra of the ligand was recorded in DMSO. The aromatic protons appear as a set of doublet, triplet and multiplets in the range of $86.8 - 7.84$ ppm, while the aliphatic protons resonate in region of $2.31 - 3.86$ ppm. All the protons are found in their expected region [29].

3.2 IR spectra

The IR spectra of Metal complexes is compared with IR spectra of ligand (L), and certain shift in band position was observed after metal complexation. Ligand (L) exhibits stretching of (C=N) stretching at 1510 cm^{-1} which on metal complexation shifts to $1480 - 1540\text{ cm}^{-1}$, suggesting that azomethine nitrogen are involved in coordination [30]. Similarly, band corresponding to C=O stretching vibration which appears at 1650 cm^{-1} in ligand L shifts to lower side $1600 - 1630\text{ cm}^{-1}$, which indicates the carbonyl oxygen in complex formation [31]. A nitrate ligand can coordinate to the metal ion in three types, as monodentate, bidentate ligand, or uncoordinated ion [32-33]. For Ln(III) complexes, the separation ($\nu_4 - \nu_1$) is approximately $145 - 165\text{ cm}^{-1}$, so in these complexes the nitrate group coordinated as bidentate ligand [32–33]. 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 $1381 - 1392\text{ cm}^{-1}$ [32-34]. Band corresponding to (M–O) bond appear in the spectra of metal ion complex at $430 - 450\text{ cm}^{-1}$, while the band corresponding to M–N appear at $365 - 390\text{ cm}^{-1}$ in metal complexes 1-7 [35]. Thus the ligand L coordinates in a neutral bidentate behaviour and coordinate to Ln(III) ion by azomethine nitrogen and carbonyl oxygen. IR spectral data also reveal that NO_3^{-1} binds to Ln(III) complexes in a bidendate 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 ligand [L] show three main absorption bands at 248, 261 and 385 nm. The band appearing at lower energy is attributed to $n - \pi^*$ transition is because 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 [36–40]. Other bands are due to $\pi - \pi^*$ of the benzene ring and $\pi - \pi^*$ transition of the azomethine group [41-42]. The UV–Vis absorption spectra of all the Ln(III) Schiff base complexes show a similar trend, which points out towards the similarity in their geometry. After complexation the bands are shifted to lower wavelength. These modifications of the shifts and intensity of the absorption bands indicates 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 [43].

3.4 Thermal Studies

Thermal results of title complexes are summarized in Table 4 (fig.6) Thermogravimetric analysis of the complexes show that all the complexes are stable up to 240°C . All the complexes undergo decomposition in two stages. Finally at 820°C respective stable lanthanide oxides are formed.

Table 1. Analytical, Conductivity and molecular weight data of lanthanide (III) Nitrate Complexes of 4[N-Isonicotinamido -4-methyl salicylaldimine (INH-MSAL)]

S.N	Complex	Found (Calcd.) % Metal	C	H	N
1	La (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	16.50 (16.63)	40.14 (40.24)	3.00 (3.11)	15.0 (15.09)
2	Pr (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	16.70 (16.83)	40.00 (40.14)	3.00 (3.10)	14.94 (15.05)
3	Nd (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	17.02 (17.16)	39.82 (39.98)	2.98 (3.09)	14.82 (14.99)
4	Sm (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	17.60 (17.76)	39.59 (39.69)	2.99 (3.07)	14.80 (14.88)
5	Gd (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	18.30 (18.42)	39.27 (39.37)	2.80 (3.04)	14.60 (14.76)
6	Tb (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	18.40 (18.58)	39.20 (39.30)	2.80 (3.04)	14.60 (14.73)
7	Dy (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	18.80 (18.92)	39.00 (39.13)	2.88 (3.02)	14.50 (14.67)

INH-MSAL-N- Isonicotinamido-4-methyl salicylaldimine (C₁₄H₁₃N₃O₂)**Table 2.1 : Infrared absorption frequencies (cm⁻¹) of Ianthanide (III) nitrate complexes of N-Isonicotinamido- 4-methyl salicylaldimine**

Assignments	(C ₁₄ H ₁₃ N ₃ O ₂)	La(NO ₃) ₃ -	Pr(NO ₃) ₃ -	Nd(NO ₃) ₃ -	Sm(NO ₃) ₃ -	Gd(NO ₃) ₃ -	Tb(NO ₃) ₃ -	Dy(NO ₃) ₃ -
	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	(C ₁₄ H ₁₃ N ₃ O ₂) ₂
1	2	3	4	5	6	7	8	9
<i>V</i> (OH)	3405m	3405m	3400	3400	3400m	3405m	3405m	3400m
	3380m	3385m	3380m	3385	3380m	3380m	3380m	3382m
<i>V</i> (NH)	3290m	3290m	3290m	3295	3290m	3295m	3295m	3290m
(asym & sym)	3220m	3220m	3220m	3220m	3225m	3222m	3220m	3220m
C-H, C=C, C-N	3150m	3130m	3135m	3145m	3130m	3160m	3130m	3130m
	3020sh	3065w	3065w	3130m	3065w	3125m	3065w	3065w
Stretching	2980s	3000w	3005w	3065w	3005w	3005w	2970m	3000w
	2960m	2980vw	2980vw	3005w	2980vh	2900sh	2930m	2980vw
	2900sh	2860w	2990w	2865w	2860w	2860w	2870w	2860w
Amide-I	1660vs	1620vs	1610Vs	1620s	1600vs, br	1600vs br	1660s	1570s
(azomethine)								
Amide-II + δ (NH)	1560s	1550w	1530vs ^a	1555m	1525m	1535sh	1530sh	1525m
	1550s	1525m					Contd.....	

Table 2.2 : Infrared absorption frequencies (cm^{-1}) of Ianthanide (III) nitrate complexes of N-Isonicotinamido- 4-methyl salicyladimine

Assignments	$(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2)$	$\text{La}(\text{NO}_3)_3^-$	$\text{Pr}(\text{NO}_3)_3^-$	$\text{Nd}(\text{NO}_3)_3^-$	$\text{Sm}(\text{NO}_3)_3^-$	$\text{Gd}(\text{NO}_3)_3^-$	$\text{Tb}(\text{NO}_3)_3^-$	$\text{Dy}(\text{NO}_3)_3^-$
		$(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2)_2$						
1	2	3	4	5	6	7	8	9
C=C, C=N br ^a	1530s	1510s, br	1480vs ^b	1525m ^b	1510sh ^b	1510s ^b	1510s ^b	1510s,
Stretching and ring vibrations (Pyridine ring)	1510sh	1500s ^b	1540vs	1510m ^b	1500s ^b	1500s ^b	1480w	1500s ^b
	1480s	1480w	---	1480vs ^b	1460	1460m	1460w	1480w
	1440vs	1460	---	1470vs	1400vs, br	1410sh	1418sh	1460m
	1400vs	1410sh	--	1425w	---	1400m	1400m	
Ring Deformation	1355s	1360s	1350s	1375m	1375m	1370m	1375m	1375m
C-H in-Plane Deformation	1305	1325m	1315m	1310m	1320s	1320m ^b	1325m	1325m
vs ^b	1315sh	1300sh ^b	1240sh	1215s	1280s	1300w	1280s	1300sh ^b
	1285	1295vs	1210s	1180m	1260m	1280m	1265m	1292
	1270s	1265m	1105sh	1140m	1235m	1260w	1240m	1265m
	1255sh	1240m		1105m	1228w	1240w	1220w	1245w
	1220m	1220w			1200w	1220w	1205vs	1220w
	1140vs	1208w			1165m	1205w	1170m	1205w
		1170w			1135s	1175w	1135m	1190sh
		1135m			1105s	1130w	1100w	1170w
		1120m				1100w		1135m
								1120m
Ring Breathing (pyridine ring)	1075w	1050m, br	1085s	1070m ^b 1050s,br ^b	1040s,br ^b	1040s,br ^b	1040s,br ^b	1050m,br ^b
	1060s	1025m	1040m ^b 1015s	1020m ^b	1020m		1025m ^b 1025m	
			1020m	1040s	1015m			

Table 2.3 : Infrared absorption frequencies (cm^{-1}) of Ianthanide (III) nitrate complexes of N-Isonicotinamido- 4-methyl salicyladimine

Assignments	$(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2)$	$\text{La}(\text{NO}_3)_3^-$	$\text{Pr}(\text{NO}_3)_3^-$	$\text{Nd}(\text{NO}_3)_3^-$	$\text{Sm}(\text{NO}_3)_3^-$	$\text{Gd}(\text{NO}_3)_3^-$	$\text{Tb}(\text{NO}_3)_3^-$	$\text{Dy}(\text{NO}_3)_3^-$
		$(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2)_2$						
1	2	3	4	5	6	7	8	9
C-H out-of-Plane deformation	980s	980s	980	970m	980sh	980sh	980w	980w
	940s	965	910w	940w	940m	945w	940w	950w
	910m	950w	885m	890m	925w	925w	930m	930w
	840m	905w	850m	860m	890m	890m	895m	905w
	760s	900w	820w ^b	820s ^b	860m	855m	850s	900w
		820m ^b	755s ^b	810s ^b	820m ^b	818m ^b	820s ^b	820m ^b
		810m ^b	700s ^b	740s ^b	810s ^b	808s ^b	810s ^b	810m ^b
		740s ^b		700s ^b	740s ^b	740s ^b	740s ^b	7404 ^a
		700w ^b			740w ^b	740w ^b	740w ^b	740w ^b
Out-of-Plane	680s	675w	540w	695w	660m	680sh	680w	675w
			620m		600sh	670m	670w	670m
					540w	610m	640w	620m
						520w	600w	560w
							600w,br	
							550w	
							520vw	
ν (Ln-O) / ν (Ln-N)	-	440w	450m,br	430w	460m	430m	455m	440w
Metal-ligand Vibration		370w	360w	360w	455m	365w	445m	370w
					360w		360w	

Table 2.4: Infrared absorption frequencies (cm^{-1}) of nitrate ion in the lanthanide (III) nitrate complexes of Schiff bases

Complexes	$(\nu_2 + \nu_5)$		$(\nu_2 + \nu_6)$		$(\nu_2 + \nu_5) -$ $(\nu_2 + \nu_6)$		ν_4	ν_5	ν_2	ν_6	ν_3	ν_5
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.		
Gd (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1788vw	1750vw	38	1510sh	1320m	1040m, br	818m	740s	700w			
				1500s	1300w	1020m						
Tb (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1780vw	1740vw	40	1500s	1325s	1040m	820s	740s	698w			
						810s						
Dy (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1790vw	1745vw	45	1510s, br	1325m	1050m, br	820m	740s	700w			
					1300sh		810m					
La (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1788vw	1736vw	52	1520s	1300s	1052m	820s	745m	720s			
Pr (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1790vw	1742vw	48	1515m	1305s	1050m	822s	740m				
Nd (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1782vw	1748vw	44	1515m	1305m	1045m	820s	745s	725s			
Sm (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1782vw	1732vw	50	1518m	1300s, br	1050m	830m	740m	725w			
Gd (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1787vw	1745vw	42	1520m	1305s, br	1052m	830m	740m	700sh			
Tb (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1786vw	1738vw	48	1510m	1300s	1050m	830m	740m	700w			
Dy (NO_3) ₃ .2 ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)	1787vw	1750vw	37	1525s	1305s	1050m	825m	745m	722w			

Table 4 : Thermoanalytical results of some Lanthanide (III) nitrate complexes of 4[(N-Isonicotinamido –4-methyl Salicylaldimine]

S.N	Complex	Sample	Residual		Ligand mass loss (%)				Residual(%)	
			Weight	Mass	240-345°C		390-470°C		Ca. 820°C	
					Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^c	Exp
1-Pr (NO_3) ₃ ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$) ₂	10.25	2.17			30.46	30.11	60.94	60.62	20.10	20.35
2-Gd (NO_3) ₃ ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$) ₂	15.10	3.34			29.88	29.62	59.78	59.54	21.24	21.49
3-Tb (NO_3) ₃ ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$) ₂	18.50	4.21			29.82	29.57	59.68	59.41	21.39	21.59
4-Dy (NO_3) ₃ ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$) ₂	12.60	2.84			29.70	29.42	59.45	59.23	21.72	21.88

a- Calculated for loss of one molecule of ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)b- Calculated for loss of two molecule of ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$)c- Calculated for lanthanide oxide, (Pr_6O_{11} , Gd_2O_3 , Tb_{407} or Dy_2O_3)

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**).

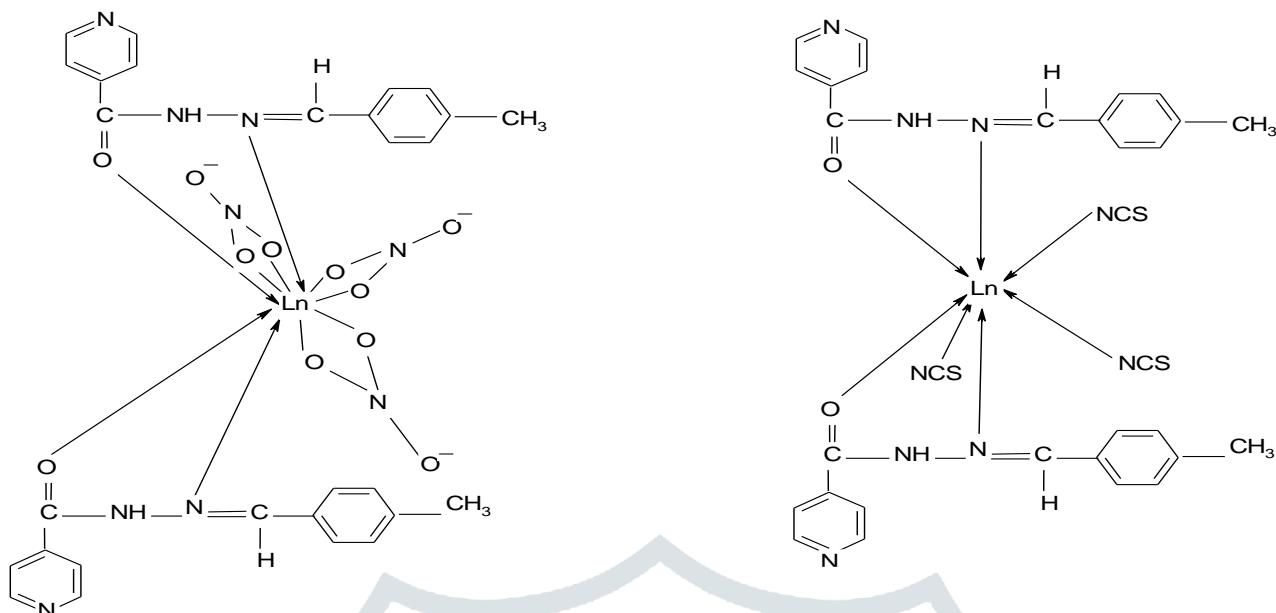


Figure 2: Proposed structure of metal complexes 1–7

4. Conclusion

In this paper we report the synthesis and characterization of Ln(III) ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb and Dy}$) 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.

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