

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 $M(NO_3)_2L_2$. 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. 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 salicylaldehyde 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 salicylaldehyde (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°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-acetyl furan 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 $\delta 6.8 - 7.84$ 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 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 ligand [L] show three main absorption bands at 248, 261 and 385 nm. The band appearing at lower energy is attributed to $n \rightarrow \pi^*$ 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 $\pi \rightarrow \pi^*$ of the benzene ring and $\pi \rightarrow \pi^*$ 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 lanthanide (III) nitrate complexes of N-Isonicotinamido- 4-methyl salicylaldimine**

Assignments	(C ₁₄ H ₁₃ N ₃ O ₂) ₂	La(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Pr(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Nd(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Sm(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Gd(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Tb(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	Dy(NO ₃) ₃ - (C ₁₄ H ₁₃ N ₃ O ₂) ₂	
	1	2	3	4	5	6	7	8	9
ν(OH)		3405m	3405m	3400	3400	3400m	3405m	3405m	3400m
		3380m	3385m	3380m	3385	3380m	3380m	3380m	3382m
ν(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	2870w	2860w	
Amide-I (azomethine)		1660vs	1620vs	1610Vs	1620s	1600vs, br	1600vs br	1660s	1570s
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	(C ₁₄ H ₁₃ N ₃ O ₂) 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
1	2	3	4	5	6	7	8	9
C=C, C= N br ^a	1530s	1510s, br	1480vs ^a	1525m ^a	1510sh ^a	1510s ^a	1510s ^a	1510s,
Stretching and ring vibrations (Pyridine ring)	1510sh 1480s	1500s ^a 1480w	1540vs ---	1510m ^a 1480vs ^a	1500s ^a 1460	1500s ^a 1460m	1480w 1460w	1500s ^a 1480w
Ring Deformation	1440vs 1400vs	1460 1410sh	---	1470vs 1425w	1400vs, br ---	1410sh 1400m	1418sh 1400m	1460m
C-H in-Plane Deformation	1355s 1305	1360s 1325m	1350s 1315m	1375m 1310m	1375m 1320s	1370m 1320m ^a	1375m 1325m	1375m 1325m
vs ^a	1315sh 1285 1270s 1255sh 1220m 1140vs	1300sh ^a 1295vs 1265m 1240m 1220w	1240sh 1210s 1105sh	1215s 1180m 1140m 1105m	1280s 1260m 1235m	1300w 1280m 1260w 1240w 1200w	1280s 1265m 1240m 1220w 1205vs	1300sh ^a 1292 1265m 1245w 1220w
Ring Breathing (pyridine ring)	1075w 1060s 1020m	1050m, br 1025m 1020m	1085s 1040m ^a 1040s	1070m ^a 1050s,br ^a 1020m ^a 1015m	1040s,br ^a 1020m	1040s,br ^a 1025m ^a 1025m	1050m,br ^a 1025m ^a	1050m,br ^a 1025m ^a

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

Assignments	(C ₁₄ H ₁₃ N ₃ O ₂) 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
1	2	3	4	5	6	7	8	9
C-H out-of Plane deformation	980s 940s 910m 840m 760s	980s 965 950w 905w 900w 820m ^a 810m ^a 740s ^a 700w ^a	980 910w 885m 850m 820w ^a 755s ^a 700s ^a	970m 940w 890m 860m 820s ^a 810s ^a 740s ^a 700s ^a	980sh 940m 925w 860m 820m ^a 810s ^a 740s ^a 740w ^a	980sh 945w 925w 890m 855m 818m ^a 808s ^a 740s ^a 740w ^a	980w 940w 930m 895m 850s 820s ^a 810s ^a 740s ^a 740w ^a	980w 950w 930w 905w 900w 820m ^a 810m ^a 740s ^a 740w ^a
Out-of-Plane	680s	675w 620m	540w	695w 660m 600sh 540w	660m 670m 610m 520w	680sh 670w 640w 600w,br 550w 520vw	680w 670m 620m 560w	675w 620m
ν (Ln-O) / ν (Ln-N)	--	440w	450m,br	430w	460m	430m	455m	440w
Metal-ligand Vibration		370w	360w	360w	455m 360w	365w	445m 360w	370w

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

Complexes	($\nu_2 + \nu_3$)	($\nu_2 + \nu_4$)	($\nu_2 + \nu_5$) - ($\nu_2 + \nu_6$)	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 (C ₁₄ H ₁₃ N ₃ O ₂)	1788vw	1750vw	38	1510sh 1500s	1320m 1300w	1040m, br 1020m	818m	740s	700w
Tb (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O ₂)	1780vw	1740vw	40	1500s	1325s	1040m	820s 810s	740s	698w
Dy (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O ₂)	1790vw	1745vw	45	1510s, br	1325m 1300sh	1050m, br	820m 810m	740s	700w
La (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1788vw	1736vw	52	1520s	1300s	1052m	820s	745m	720s
Pr (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1790vw	1742vw	48	1515m	1305s	1050m	822s	740m	
Nd (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1782vw	1748vw	44	1515m	1305m	1045m	820s	745s	725s
Sm (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1782vw	1732vw	50	1518m	1300s, br	1050m	830m	740m	725w
Gd (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1787vw	1745vw	42	1520m	1305s, br	1052m	830m	740m	700sh
Tb (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	1786vw	1738vw	48	1510m	1300s	1050m	830m	740m	700w
Dy (NO ₃) ₃ .2 (C ₁₄ H ₁₃ N ₃ O)	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 Weight (mg)	Residual Mass (mg)	Ligand mass loss (%)				Residual(%)	
				240-345°C		390-470°C		Ca. 820°C	
				Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^c	Exp
1-Pr (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	10.25	2.17	30.46	30.11	60.94	60.62	20.10	20.35	
2-Gd (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	15.10	3.34	29.88	29.62	59.78	59.54	21.24	21.49	
3-Tb (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ O ₂) ₂	18.50	4.21	29.82	29.57	59.68	59.41	21.39	21.59	
4-Dy (NO ₃) ₃ (C ₁₄ H ₁₃ N ₃ 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 (C₁₄H₁₃N₃O₂)

b- Calculated for loss of two molecule of (C₁₄H₁₃N₃O₂)

c- Calculated for lanthanide oxide, (Pr₆O₁₁, Gd₂O₃, Tb₄O₇ or Dy₂O₃)

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**).

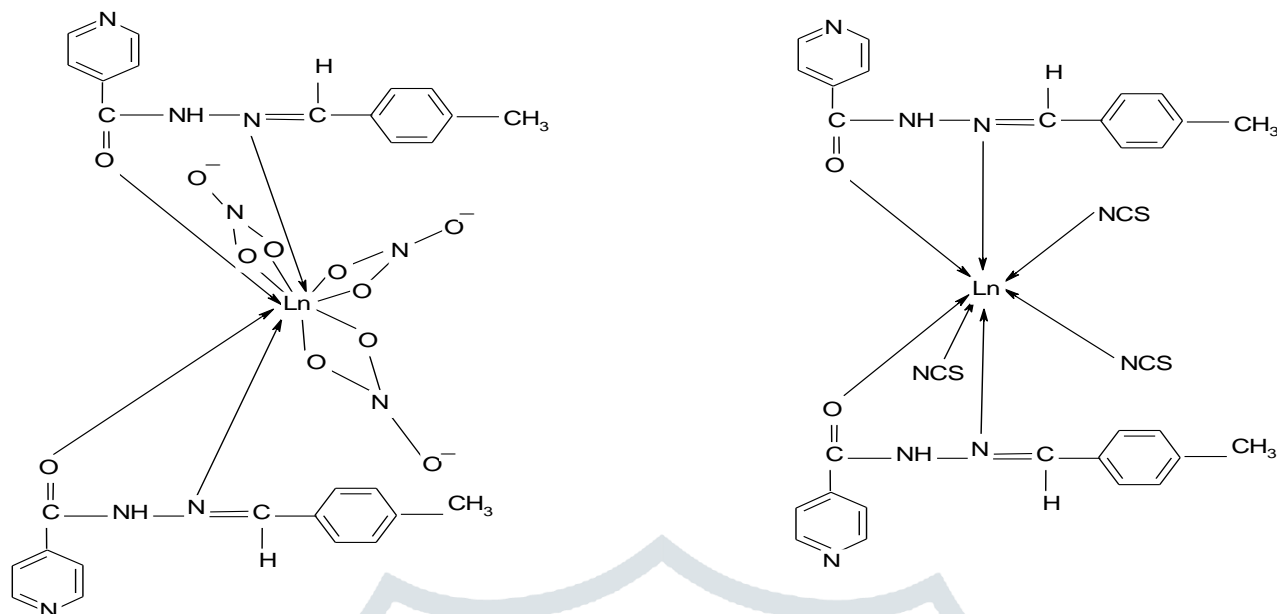


Figure 2: Proposed structure of metal complexes 1–7

4. Conclusion

In this paper we report the synthesis and characterization of Ln(III) (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.

References

1. N. Sabbatini, M. Guardigli, and J. M. Lehn, "Luminescent lanthanide complexes as photochemical supramolecular devices," *Coordination Chemistry Reviews*, vol. 123, no. 1-2, pp. 201–228, 1993. [View at Google Scholar](#) · [View at Scopus](#)
2. P. A. Vigato and S. Tamburini, "The challenge of cyclic and acyclic schiff bases and related derivatives," *Coordination Chemistry Reviews*, vol. 248, no. 17-20, pp. 1717–2128, 2004. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
3. V. Alexander, "Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides," *Chemical Reviews*, vol. 95, no. 2, pp. 273–342, 1995. [View at Google Scholar](#) · [View at Scopus](#)
4. C. Benelli and D. Gatteschi, "Magnetism of lanthanides in molecular materials with transition-metal ions and organic radicals," *Chemical Reviews*, vol. 102, no. 6, pp. 2369–2387, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
5. A. Døssing, "Luminescence from lanthanide(3+) ions in solution," *European Journal of Inorganic Chemistry*, no. 8, pp. 1425–1434, 2005. [View at Publisher](#) · [View at Google Scholar](#)
6. J. C. G. Bünzli and C. Piguet, "Lanthanide-containing molecular and supramolecular polynuclear functional assemblies," *Chemical Reviews*, vol. 102, no. 6, pp. 1897–1928, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
7. A. D. Sherry and C. F. G. C. Geraldes, "Lanthanide probes in life: chemical and earth sciences," in *Theory and Practice*, G. R. Choppin, Ed., vol. 93, Elsevier, Amsterdam, The Netherlands, 1989. [View at Google Scholar](#)
8. D. Parker, R. S. Dickins, H. Puschmann, C. Crossland, and J. A. K. Howard, "Being excited by lanthanide coordination complexes: aqua species, chirality, excited-state chemistry, and exchange dynamics," *Chemical Reviews*, vol. 102, no. 6, pp. 1977–2010, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
9. M. Taniguchi and K. Takahei, "Optical properties of the dominant Nd center in GaP," *Journal of Applied Physics*, vol. 73, no. 2, pp. 943–947, 1993. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
10. J. P. Costes, F. Dahan, A. Dupuis, and J. P. Laurent, "A general route to strictly dinuclear Cu(II)/Ln(III) complexes. Structural determination and magnetic behavior of two Cu(II)/Gd(III) complexes," *Inorganic Chemistry*, vol. 36, no. 16, pp. 3429–3433, 1997. [View at Google Scholar](#) · [View at Scopus](#)
11. A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, and D. Gatteschi, "Crystal and molecular structure of and magnetic coupling in two complexes containing gadolinium(III) and copper(II) ions," *Journal of the American Chemical Society*, vol. 107, no. 26, pp. 8128–8136, 1985. [View at Google Scholar](#) · [View at Scopus](#)
12. J. Lisowski and P. Starynowicz, "Heterodinuclear macrocyclic complexes containing both nickel(II) and lanthanide(III) ions," *Inorganic Chemistry*, vol. 38, no. 6, pp. 1351–1355, 1999. [View at Google Scholar](#) · [View at Scopus](#)
13. V. Alexander, "Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides," *Chemical Reviews*, vol. 95, no. 2, pp. 273–342, 1995. [View at Google Scholar](#) · [View at Scopus](#)

14. V. De Zea Bermudez, R. A. Sá Ferreira, L. D. Carlos, C. Molina, K. Dahmouche, and S. J. L. Ribeiro, "Coordination of Eu^{3+} ions in siliceous nanohybrids containing short polyether chains and bridging urea cross-links," *Journal of Physical Chemistry B*, vol. 105, no. 17, pp. 3378–3386, 2001. [View at Google Scholar](#) · [View at Scopus](#)
15. C. Reinhard and H. U. Güdel, "High-resolution optical spectroscopy of $\text{Na}_3[\text{Ln}(\text{dpa})_3] \cdot 13\text{H}_2\text{O}$ with $\text{Ln} = \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}$," *Inorganic Chemistry*, vol. 41, no. 5, pp. 1048–1055, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
16. C. V. K. Sharma and R. D. Rogers, "Molecular chinese blinds': Self-organization of tetranitrato lanthanide complexes into open, chiral hydrogen-bonded networks," *Chemical Communications*, no. 1, pp. 83–84, 1999. [View at Publisher](#) · [View at Google Scholar](#)
17. Y. Liang, R. Cao, W. Su, M. Hong, and W. Zhang, "Syntheses, structures, and magnetic properties of two gadolinium (III)—Copper (II) coordination polymers by a hydrothermal reaction," *Angewandte Chemie—International Edition*, vol. 39, no. 18, pp. 3304–3307, 2000. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
18. Y. Liang, M. Hong, W. Su, R. Cao, and W. Zhang, "Preparations, structures, and magnetic properties of a series of novel copper(II)-lanthanide(III) coordination polymers via hydrothermal reaction," *Inorganic Chemistry*, vol. 40, no. 18, pp. 4574–4582, 2001. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
19. R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi, and Q. Shi, "Syntheses and characterizations of three-dimensional channel-like polymeric lanthanide complexes constructed by 1,2,4,5-benzenetetracarboxylic acid," *Inorganic Chemistry*, vol. 41, no. 8, pp. 2087–2094, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
20. Z. Wang, C.-M. Jin, T. Shao et al., "Syntheses, structures, and luminescence properties of a new family of three-dimensional open-framework lanthanide coordination polymers," *Inorganic Chemistry Communications*, vol. 5, no. 9, pp. 642–648, 2002. [View at Publisher](#) · [View at Google Scholar](#)
21. L. Pan, X. Huang, J. Li, Y. Wu, and N. Zheng, "Novel single- and double-layer and three-dimensional structures of rare-Earth metal coordination polymers: the effect of lanthanide contraction and acidity control in crystal structure formation," *Angewandte Chemie—International Edition*, vol. 39, no. 3, pp. 527–530, 2000. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
22. J. P. Costes, J. M. Clemente, F. Dahan, F. Nicodème, and M. Verelst, "Unprecedented ferromagnetic interaction in homobinuclear erbium and gadolinium complexes: structural and magnetic studies," *Angewandte Chemie—International Edition*, vol. 41, no. 2, pp. 323–325, 2002. [View at Publisher](#) · [View at Google Scholar](#) · [View at Scopus](#)
23. A. Ouchi, Y. Suzuki, Y. Ohki, and Y. Koizumi, "Structure of rare earth carboxylates in dimeric and polymeric forms," *Coordination Chemistry Reviews*, vol. 92, pp. 29–43, 1988. [View at Google Scholar](#) · [View at Scopus](#)
24. A. Panagiotopoulos, T. F. Zafriopoulos, S. P. Perlepes et al., "Molecular structure and magnetic properties of acetato-bridged lanthanide(III) dimers," *Inorganic Chemistry*, vol. 34, no. 19, pp. 4918–4920, 1995. [View at Google Scholar](#) · [View at Scopus](#)
25. F. Aydogan, N. Öcal, Z. Turgut, and C. Yolacan, "Transformations of aldimines derived from pyrrole-2-carbaldehyde. Synthesis of thiazolidino-fused compounds," *Bulletin of the Korean Chemical Society*, vol. 22, no. 5, pp. 476–480, 2001. [View at Google Scholar](#) · [View at Scopus](#)
26. M. A. V. Ribeiro Da Silva, M. D. M. C. Ribeiro Da Silva, M. J. S. Monte, J. M. Gonçalves, and E. M. R. Fernandes, "Energetics of metal-ligand binding in copper(II) and nickel(II) complexes of two Schiff bases," *Journal of the Chemical Society—Dalton Transactions*, no. 7, pp. 1257–1262, 1997. [View at Google Scholar](#) · [View at Scopus](#)
27. J. Yao, W. Dou, W. Liu, J. Zheng, *Inorg. Chem. Commun.* 12(2009)430
28. V. Alexander, "Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides," *Chemical Reviews*, 95, (1995) 273–342.
29. V. De Zea Bermudez, R. A. Sá Ferreira, L. D. Carlos, C. Molina, K. Dahmouche, and S. J. L. Ribeiro, "Coordination of Eu^{3+} ions in siliceous nanohybrids containing short polyether chains and bridging urea cross-links," *Journal of Physical Chemistry B*, 105, (2001) 3378–3386.
30. C. Reinhard and H. U. Güdel, "High-resolution optical spectroscopy of $\text{Na}_3[\text{Ln}(\text{dpa})_3] \cdot 13\text{H}_2\text{O}$ with $\text{Ln} = \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}$," *Inorganic Chemistry*, 41(2002) 1048–1055.
31. C. V. K. Sharma and R. D. Rogers, "Molecular chinese blinds': Self-organization of tetranitrato lanthanide complexes into open, chiral hydrogen-bonded networks," *Chemical Communications*, 1(1999) 83–84.
32. S. Kumar, D. N. Dhar, P. N. Saxena, "Applications of metal complexes of Schiff bases-A review" *J. Sci. Ind. Res.*, 68, (2009) 181–187.
33. Y. Liang, R. Cao, W. Su, M. Hong, and W. Zhang, "Syntheses, structures, and magnetic properties of two gadolinium (III)—Copper (II) coordination polymers by a hydrothermal reaction," *Angewandte Chemie—International Edition*, 39, (2000) 3304–3307.
34. Y. Liang, M. Hong, W. Su, R. Cao, and W. Zhang, "Preparations, structures, and magnetic properties of a series of novel copper(II)-lanthanide(III) coordination polymers via hydrothermal reaction," *Inorganic Chemistry*, 40, (2001) 4574–4582.
35. R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi, and Q. Shi, "Syntheses and characterizations of three-dimensional channel-like polymeric lanthanide complexes constructed by 1,2,4,5-benzenetetracarboxylic acid," *Inorganic Chemistry*, 41, (2002) 2087–2094.
36. Z. Wang, C.-M. Jin, T. Shao et al., "Syntheses, structures, and luminescence properties of a new family of three-dimensional open-framework lanthanide coordination polymers," *Inorganic Chemistry Communications*, 5, (2002) 642–648.
37. L. Pan, X. Huang, J. Li, Y. Wu, and N. Zheng, "Novel single- and double-layer and three-dimensional structures of rare-Earth metal coordination polymers: the effect of lanthanide contraction and acidity control in crystal structure formation," *Angewandte Chemie—International Edition*, 39 (2000) 527–530.

- 38 J. P. Costes, J. M. Clemente, F. Dahan, F. Nicodème, and M. Verelst, "Unprecedented ferromagnetic interaction in homobinuclear erbium and gadolinium complexes: structural and magnetic studies," *Angewandte Chemie—International Edition*, 41, (2002) 323–325.
- 39 A. Ouchi, Y. Suzuki, Y. Ohki, and Y. Koizumi, "Structure of rare earth carboxylates in dimeric and polymeric forms," *Coordination Chemistry Reviews*, 92, (1988) 29–43.
- 40 A. Panagiotopoulos, T. F. Zafropoulos, S. P. Perlepes et al., "Molecular structure and magnetic properties of acetato-bridged lanthanide(III) dimers," *Inorganic Chemistry*, 34, (1995) 4918–4920.
- 41 F. Aydogan, N. Öcal, Z. Turgut, and C. Yolacan, "Transformations of aldimines derived from pyrrole-2-carbaldehyde. Synthesis of thiazolidino-fused compounds," *Bulletin of the Korean Chemical Society*, 22, (2001) 476–480.
- 42 M. A. V. Ribeiro Da Silva, M. D. M. C. Ribeiro Da Silva, M. J. S. Monte, J. M. Gonçalves, and E. M. R. Fernandes, "Energetics of metal-ligand binding in copper(II) and nickel(II) complexes of two Schiff bases," *Journal of the Chemical Society—Dalton Transactions*, 7, (1997) 1257–1262.
- 43 B.-D. Wang, Z.-Y. Yang, D.-W. Zhang, and Y. Wang, "Synthesis, structure, infrared and fluorescence spectra of new rare earth complexes with 6-hydroxy chromone-3-carbaldehyde benzoyl hydrazone," *Spectrochimica Acta A*, 63, (2006) 213–219.

