
Synthesis and Spectral Characterization of Ln(III) Complexes of Schiff base Derived from 4-Aminoantipyrine and 2-Acetylfuran

Dr Meenu Sharma^a and Dr T R Sharma (Retired Reader) Guide

Department of Chemistry, K G K (PG) College Moradabad

M J P Rohilkhand University Bareilly

Dr Sulekh Chandra

Department of Chemistry, Zakir Husain Delhi College, University of Delhi, JLN-Marg, New Delhi, India

Abstract

Ln(III) (La, Pr, Nd, Sm, Gd, Tb and Dy) complexes of Schiff base ligand L derived from 4-aminoantipyrine and 2-acetylfuran was synthesized and characterized. The synthesized complexes are non electrolytic in nature as indicated by their molar conductance value and have the general composition $Ln(NO_3)_3L_2$. The synthesized complexes was 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. Non electrolytic nature of metal complexes reveal that all the three nitrate are inside the coordination sphere. Thus lanthanide ions are surrounded by eight oxygen atom and two nitrogen atom and hence show a coordination number of 10 in the synthesized complexes.

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

1 Introduction

Schiff base represents an important group of organic ligand which are very commonly used for the preparation of coordination compounds [1]. They also show interesting physical or chemical properties due to their favorable electronic and coordination properties and the ability to act as multidentate chelating or bridging ligands. Not only this, they also show a wide range of biological activities like antimicrobial, antiradical, antidiabetic, anticancer, etc. [2–10]. Lanthanide complexes of Schiff base represents another class of compounds that show very interesting properties like luminescent properties [11–13], magnetic properties (e.g., single molecule, or single chain magnetism) [14,15] and promising biological properties (e.g., antimicrobial, or anticancer) [11–13].

Lanthanide complexes also play a very vital role in field of biomedicine as they are used as MRI contrast agents in biomedical analysis [14]. Their special photophysical and biological properties make them useful as biological probes in the areas of clinical chemistry and molecular biology [15]. Lanthanide complexes have inspired researchers not only due to their electronic configuration, but also because of the potential anticancer and antimicrobial agents [16–20]. It has been shown that ligands containing both N and O donor atoms are good building blocks for the formation of various lanthanide coordination compounds.

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. Some of the Schiff base complexes containing N and O donor atoms are effective as stereospecific catalysts for oxidation, reduction, hydrolysis, biocidal activity, and other organic and inorganic transformations. Schiff base complexes derived from amino acids are important due to their ability to possess unusual configurations and biological importance. Lanthanide Schiff base complexes have some advantages for luminescence research because of their special structures.

Prompted by these applications, in this work, bidentate Schiff base ligand L (4-[(N-2-acetyl Furan)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 (^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 2-acetyl furan (1mmole, 0.110 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 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%). 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-2-acetyl furan)amino]-antipyrine (L) (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 as shown in **Figure 1**.

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

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 $4.1\text{--}5.7\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, which indicates their non electrolytic behavior [21].

Table 1: Physical and analytical data of the ligand L and Ln(III) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy) complexes of Schiff base ligand L

No.	Molecular formula	Ω_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Yield (%)	Elemental Analysis (%) found (calc.)		
				C	H	N
L	$\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$	-	85	69.09 (69.14)	7.78 (5.80)	14.19 (14.23)
1	$\text{La}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	5.2	62	44.40 (44.60)	3.60 (3.74)	13.60 (13.77)
2	$\text{Pr}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	5.6	67	44.42 (44.49)	3.60 (3.70)	13.60 (13.74)
3	$\text{Nd}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	5.7	59	44.20 (44.34)	3.59 (3.72)	13.62 (13.69)
4	$\text{Sm}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	5.3	65	43.90 (44.05)	3.56 (3.70)	13.48 (13.60)
5	$\text{Gd}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	4.9	72	43.60 (43.73)	3.54 (3.67)	13.35 (13.50)
6	$\text{Tb}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	4.8	58	43.50 (43.65)	3.50 (3.66)	13.30 (13.47)
7	$\text{Dy}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	4.1	55	43.37 (43.48)	3.50 (3.65)	13.28 (13.42)

3.1 ¹H NMR

The ¹H 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 δ 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 [22].

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 1590 cm⁻¹ which on metal complexation shifts to 1530–1580 cm⁻¹, suggesting that azomethine nitrogen are involved in coordination [23]. Similarly, band corresponding to C=O stretching vibration which appears at 1650 cm⁻¹ in ligand L shifts to lower side 1600–1630 cm⁻¹, which indicates the carbonyl oxygen in complex formation [24]. A nitrate ligand can coordinate to the metal ion in three types, as monodentate, bidentate ligand, or uncoordinated ion [25–26]. For Ln(III) complexes, the separation ($\nu_4 - \nu_1$) is approximately 145–165 cm⁻¹, so in these complexes the nitrate group coordinated as bidentate ligand [27–28]. 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 cm⁻¹ [27–28]. Band corresponding to (M–O) bond appear in the spectra of metal ion complex at 430 – 450 cm⁻¹, while the band corresponding to M–N appear at 365 – 390 cm⁻¹ in metal complexes 1-7 [28]. 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 NO₃⁻¹ 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 π^* 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 [29–33]. Other bands are due to $\pi\pi^*$ of the benzene ring and $\pi\pi^*$ transition of the azomethine group [34–35]. 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 [36].

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

Assignment	L	1	2	3	4	5	6	7
C-H, C=C, C-N	3120m	3070w	3075w	3070w	3070w	3075w	3075w	3075w
Stretching	3080s	3015w	3025w	3025w	3020vw	3025w	3025w	3015w
	2960m	2980w	2980w	2980w	2980w	2985w	2985w	2980w
	2920w	2940w	2940w	2947w	2960w	2940w	2945w	2940w
	2100vw	2830w	2830w		2850w	2845w	2830w	2840w
	1960vw							
	1900w							
(C=O)stretching	1650vs	1630m	1620m	1620m	1600s	1620m	1610m	1600vs
(Pyrazolone)		1602w	1600m	1605m		1602w	1600sh	
(C=N)stretching	1590s	1580s	1530m	1530m	1560m	1530m	1530m	1560m
(azomethine)			1565sh		1540sh			1510sh
Ring stretching	1510vs	1485s ^a	1500m ^a	1485s,br ^a	1485s,br ^a	1490s,br ^a	1505sh ^a 1500sh ^a	
Of 5-membered	1490m	1470sh	1485s ^a	1460sh	1470sh	1470sh	1480s ^a 1400s,br ^a	
Ring		1450m	1440sh	1455sh	1455w			
CH ₃ – deformation	1420m	1425w	1420w	-----	1415w	1420w	-----	1415m
		1400w	1410w					

Assignment	L	1	2	3	4	5	6	7
Ring stretching	1360m 1340m 1300s	1380m 1340m 1300s ^a	1385s 1360sh 1305s	1390s 1375sh 1310m ^a	1385s 1360sh 1305s ^a	1385s 1360sh 1305s ^a	1390s 1370sh 1320s,br ^a 1310m ^a	1385s
N-Phenyl Stretching	1260m 1240vw 1220m 1160w	1240vs 1210sh 1195vw 1170w 1160m	1245vs 1210sh 1160vw 1170w 1160m	1250m 1170sh	1240m 1160m	1250m 1170m	1255m 1170m 1210sh 1160m	1240m
In- plane blending of CH-N-CH ₃ Stretching	1130m 1120s	1140sh 1130m 1102w	1130sh 1105w	1110w	1110w 1105w	1110w 1100w	1110w 1105w	1110w 1105w
CH ₃ - Rocking	1080m 1050w 1020s	1075m 1025s ^a	1070m 1030s ^a 1030m ^a	180m 1050vw 1025s ^a	1070w 1070m 1075m 1070vw	1070w 1070m 1075m 1070vw	1070vw 1050vw 1025s ^a	1050vw 1025s ^a
Ring breathing of benzene	1000m 980sh	975m 960sh	965m	970m	980vw 960w	970m	970m	965m 960w
C-H out-of-plane Deformation of Pyrazolone ring	970m 940w 920m	930w 910vw	930w 915w	930w 920w	930w 910vw 910vw 910vw	935w	930w 910vw	930w

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

No.	Compound	λ_{\max} (nm)	Band Assignment
L	$C_{17}H_{17}N_3O_2$	248, 261, 385	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
1	$La(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	222, 244, 339	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
2	$Pr(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	225, 244, 335	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
3	$Nd(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	221, 241, 329	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
4	$Sm(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	223, 245, 338	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
5	$Gd(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	220, 241, 331	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
6	$Tb(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	220, 244, 338	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$
7	$Dy(NO_3)_3(C_{17}H_{17}N_3O_2)_2$	235, 249, 345	$n \rightarrow \pi$ $\pi \rightarrow \pi^*$

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 final residues left are rare earth oxides. The results are tabulated in **Table 4**. All the complexes undergo three steps decomposition and showing similar trend leaving metal oxide as residue. The first step in the range of $110\text{--}235^{\circ}\text{C}$ initial weight loss corresponds to the loss of the coordinated nitrate group and some organic fragments while second step in the temperature range $235\text{--}475^{\circ}\text{C}$ corresponds to loss of organic moiety. In the final step in range of $495\text{--}800^{\circ}\text{C}$, 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	$\text{La}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	120–235	La_2O_3	18.25	35.61		
		2 nd	235–475		19.32			
		3 rd	475–800		26.88			
2	$\text{Pr}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	120–235		Pr_2O_3		21.74	35.98
		2 nd	235–460				19.68	
		3 rd	460–830				22.73	
3	$\text{Nd}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	120–230	Nd_2O_3		18.98	36.08	
		2 nd	230–465			21.72		
		3 rd	465–790			23.36		
4	$\text{Sm}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	110–230		Sm_2O_3	20.23		38.01
		2 nd	230 – 475			21.12		
		3 rd	475 – 820			20.74		
5	$\text{Gd}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	120–235	Gd_2O_3		18.34	38.97	
		2 nd	235–475			21.76		
		3 rd	475–800			21.05		
6	$\text{Tb}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	110–230		Tb_2O_3	20.16		39.14
		2 nd	230–475			19.56		
		3 rd	475–790			21.30		
7	$\text{Dy}(\text{NO}_3)_3(\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2)_2$	1 st	115–235	Dy_2O_3		22.12	40.04	
		2 nd	235–465			17.45		
		3 rd	465–800			20.46		

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

Ln(III) (Ln = La, Pr, Nd, Sm, Gd, Tb and Dy) complexes of the Schiff base (**4-[(N-2-acetyl)amino]antipyrine**) was synthesized and characterized. The structure of the synthesized ligand and complexes was thoroughly studied by various analytical and spectroscopic techniques like elemental analysis, ¹H NMR, IR, UV-Vis and TGA. The values of molar conductance predict that the synthesized complexes are non-electrolytic in nature. The complexes were found to be stable at room temperature. On the basis of the spectroscopic data it was concluded that nitrate coordinate in a bidentate fashion, thus in total 8 oxygen atom (6 from nitrate and two from carbonyl oxygen) and two azomethine nitrogen binds to Ln(III) ions.

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