

Synthesis, Characterization and Antimicrobial Activity of Schiff Base Ligand Complexes of Sm(III), Gd(III) and Dy(III) ions

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Abstract: The Gd(III), Dy(III) and Sm(III) complexes of Schiff base derived from acetoacetanilide and 1,3-diaminopropane, $[MX_3(LH_2)]$, where $X = Cl^-, NO_3^-, NCS^-$, have been synthesized in alcohol and characterized by elemental analysis, electrical conductance in non-aqueous solvents, spectral as well as magnetic susceptibility measurements. In these complexes, ligand LH_2 acts as a tetradentate ligand coordinating through the two azomethine nitrogen atoms and the two enolizable carbonyl group of acetoacetanilide moiety. The molar conductance of the complexes in DMF and DMSO are in the range of non-electrolytes. The antimicrobial activities of the ligand and their metal complexes were screened by agar diffusion method and found that the metal complexes have higher antimicrobial activity than the free ligand.

Key Words: Acetoacetanilide, 1,3-diaminopropane, Schiff base.

Introduction

A Schiff base ligand represents one of the most widely utilized classes of ligands in metal coordination chemistry. Synthesis of tetradentate Schiff base ligands by reaction between diamines and a corresponding salicylaldehyde derivative is an important reaction in organic chemistry, due to the great number of molecules that can be generated and well-known ability of these tetradentate ligands to form stable complexes with different cations. The literature reveals that Schiff base ligands are excellent coordinating ligands because of the high stability of the coordination compounds, their good solubility in common solvents and the flexibility in varying the chemical environment about the C=N group. The $C=N$ system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well [1]. The present work is the study of Gd(III), Dy(III) and Sm(III) metal complexes of the Schiff base derived from acetoacetanilide and 1,3-diaminopropane. Synthesis, Characterization and antimicrobial activities of above metal complexes are reported here.

Experimental

Metal salts, acetoacetanilide, 1,3-diaminopropane and other reagents were AR grade. Solvents such as ethanol, methanol and acetone were purified by standard procedures [2]. C,H and N were estimated by using elemental analyser, elementar Vario EL III. The metal estimations were carried out by oxalate-oxide method [3]. The IR spectra of the Schiff base and its metal complexes were recorded on a FTIR Shimadzu spectrophotometer in the $4000-400\text{ cm}^{-1}$ region in KBr powder. The electronic spectra of the complexes were

recorded in HPLC grade DMF and DMSO on a Shimadzu spectrophotometer in the region of 800-200 nm. Molar conductivity measurements were recorded on systronic conductivity meter type 304. Magnetic measurements of the complexes were performed on a Magway MSB Mk 1 susceptibility balance at room temperature. Thermal decomposition studies were recorded in a static nitrogen atmosphere with a heating rate of 10⁰C/min, using diamond TG/DTA thermogravimetric/ differential thermal analyzer.

Synthesis of the ligand

The Ligand(LH₂) was prepared by the condensation of acetoacetanilide and 1,3-diaminopropane in 2:1 molar ratio by refluxing in acetone [4].

Preparation of metal complexes

The lanthanide(III) chlorides, nitrates and thiocyanates were synthesized by following the general method. To a hot methanolic solution of the ligand LH₂ (0.001 mol), a methanolic solution of the Ln(III) salt (0.001 mol) was added dropwise with constant stirring. The pH of the mixture was adjusted to 7- 8 by adding 10% alcoholic ammonia solution and again refluxed the mixture for 10- 12 hours more. The resulting solution was concentrated to one third and kept overnight. The precipitated metal complex was filtered, washed with methanol and finally dried in a *vacuum* desiccator over calcium chloride.

Results and Discussion

All the complexes are stable at room temperature and non-hygroscopic. They are insoluble in common organic solvents like ether, acetone, benzene, carbon tetrachloride and nitrobenzene but are freely soluble in DMF and DMSO. Lanthanum(III) complexes are purple or reddish in colour. The analytical data and empirical formulae of the complexes are presented in Table 1. The data indicates 1:1 molar ratio of the metal and the ligand and the complexes can be represented as [Ln(LH₂) X₃] where Ln = Sm, Gd or Dy and X = Cl⁻, NO₃⁻, NCS⁻.

Table 1: Elemental and other physico- chemical data of LH₂ and its complexes

Compound	M.P °C	Colour	Found(Calcd.)%					μ _{eff} (BM)
			M	C	H	N	Cl/S	
[Sm(LH ₂)(Cl) ₃]	286	Greenish white	23.48 (23.16)	42.76 (42.55)	4.44 (4.35)	8.38 (8.63)	16.35 (16.38)	1.54
[Sm(LH ₂)(NO ₃) ₃]	288	Dirty white	20.68 (20.63)	36.83 (37.90)	3.57 (3.87)	13.52 (13.45)	--	1.63
[Sm(LH ₂)(NCS) ₃]	279	Dirty white	21.23 (20.97)	43.29 (43.55)	4.12 (3.94)	13.38 (13.67)	12.90 (13.41)	1.66
[Gd(LH ₂)(Cl) ₃]	294	Reddish yellow	24.34 (23.97)	42.22 (42.10)	4.52 (4.30)	8.37 (8.54)	16.14 (16.21)	7.78
[Gd(LH ₂)(NO ₃) ₃]	295	Reddish yellow	21.65 (21.37)	37.85 (37.55)	3.66 (3.84)	13.42 (13.33)	--	7.85
[Gd(LH ₂)(NCS) ₃]	286	Reddish yellow	22.02 (21.72)	43.72 (43.13)	3.65 (3.90)	13.38 (13.54)	12.89 (13.29)	7.14
[Dy(LH ₂)Cl ₃]	292	Reddish brown	23.96 (24.57)	41.43 (41.77)	4.65 (4.27)	8.71 (8.47)	16.42 (16.08)	10.53
[Dy(LH ₂)(NO ₃) ₃]	290	Light brown	22.06 (21.93)	36.98 (37.28)	3.63 (3.81)	13.25 (13.23)	--	10.67
[Dy(LH ₂)(NCS) ₃]	290	Light brown	22.15 (22.28)	42.68 (42.82)	3.24 (3.66)	13.76 (13.45)	13.83 (13.19)	10.55

Electrical conductance

The molar conductance values of 10^{-3} M solutions of the complexes of gadolinium, dysprosium and samarium in two non aqueous solvents, DMF and DMSO are respectively in the range of 12.8- 15.6 and 7.6-9.8 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. These observed values of the metal complexes indicate the non-electrolytic nature [5].

Magnetic behaviour

The magnetic moment values of the complexes are presented in Table 1. All the lanthanide complexes synthesized were paramagnetic and the observed magnetic moment values of Gd(III) (7.14-7.85 BM) and Dy(III) (10.53-10.67 BM) complexes except that of Sm(III) showed only very little deviation from the calculated values of the lanthanide ions. This indicates that the 4f electrons are not much disturbed by the ligand field produced by the Schiff bases. The deviation of the magnetic moment values of Sm(III) complexes (1.54-1.66 BM) could be attributed to low J-J separation, which leads to the thermal population of higher energy levels [6,7].

Infrared spectra

The characteristic IR frequencies of the ligand LH₂ and its complexes along with their assignments are listed in Table 2. Bands due to –OH and –C=N are distinguishable and provide evidence regarding the structure of the ligand and its bonding with metal. A band at 1591 cm^{-1} in the ligand is attributed to –C=N stretching vibration. On coordination, this band is shifted to

lower frequency by 7-22 cm^{-1} . The negative shift of this band is a clear indication of the participation of the azomethine nitrogen atoms in complex formation[8,9,10].

Table 2: Important IR spectral bands of LH₂ and its lanthanide(III) complexes

Compound	(C=N) cm^{-1}	(C- O) cm^{-1}	(M-O) cm^{-1}	(M-N) cm^{-1}
LH ₂	1591	1251	-	-
[Sm(LH ₂)(Cl ₃)]	1575	1259	414	535
[Sm(LH ₂)(NO ₃) ₃]	1578	1261	416	536
[Sm(LH ₂)(NCS) ₃]	1569	1262	420	524
[Gd(LH ₂)Cl ₃]	1584	1260	425	510
[Gd(LH ₂)(NO ₃) ₃]	1583	1258	421	510
[Gd(LH ₂)(NCS) ₃]	1576	1262	418	512
[Dy(LH ₂)Cl ₃]	1581	1261	420	524
[Dy(LH ₂)(NO ₃) ₃]	1582	1264	421	525
[Dy(LH ₂)(NCS) ₃]	1577	1259	416	520

This is supported by the appearance of band at 510-536 cm^{-1} corresponding to the stretching vibration of M–N bond. Bands at 414-425 cm^{-1} correspond to M–O stretching vibrations. Band at 3305 cm^{-1} observed in the ligand is due to stretching vibrations of free –OH. In the complexes, this frequency is downshifted to 3240–3280 cm^{-1} indicating a weakening of –OH bond due to coordination through enolic –OH. The coordination by enolic OH group is in a different manner. The enolic oxygen was coordinated to the metal ion without deprotonation. The stretching vibration of enolic C–O observed at 1251 cm^{-1} in the ligand shows a positive shift by 8-13 cm^{-1} in complexes indicate bond formation[11]. The nitrate complexes of samarium(III), gadolinium(III) and dysprosium(III) show characteristic vibrational frequencies of the coordinated nitrate ions. The infrared spectra of nitrate complexes revealed two additional strong bands around 1430 cm^{-1} and 1310 cm^{-1} which were not present in the ligand. These could be attributed to ν_4 and ν_1 vibrations, respectively, of the coordinated nitrate ion. The magnitude of separation of these bands is around 110 cm^{-1} , which indicates that the nitrate ion is coordinated to the metal ion in a monodentate fashion [11]. The combination frequency observed in the region 1700-1800 cm^{-1} of the infrared spectrum corresponds to ($\nu_1 + \nu_4$) for a monodentate coordination and are in good agreement with the suggested value of Lever *et al* [12]. The medium band around 1073 cm^{-1} due to the ν_2 vibrations of the nitrate is an additional evidence for the presence of coordinated nitrate ion [13]. In the chloride complexes the chloride ions are also coordinated to the metal ion as evidenced by the non electrolytic nature of the complexes.

The lanthanide thiocyanate complexes show strong IR bands around 2060-2070 cm^{-1} attributed to the (C-N) stretching frequency. The position and intensity of these bands suggests the N-bonded nature of the thiocyanate group. This lies on the boarder line for distinguishing between sulphur and nitrogen bonding in the thiocyanate. The (C-S) bond identified in the region 780-840 cm^{-1} attests the above inference. The (NCS) is also identified in the region 470-480 cm^{-1} [14].

Electronic spectra

The f orbitals in Ln^{3+} species are deep inside the metal; therefore, the crystal field effects are very much smaller in the lanthanide complexes compared to those in the d series of metals[4]. The electronic spectra of the complexes in DMSO exhibit the two spectral bands in the regions at 250-257 nm (40000-38911 cm^{-1}) and 352-359 nm (28409-27855 cm^{-1}), which are very close to those observed in the spectrum of the ligand. Compared with the electronic spectrum of the ligand, there is a shift to lower frequency, which further confirms the formation of complexes.

Thermogravimetric analysis

All complexes were studied by thermodynamic analysis from ambient temperature to 700 $^{\circ}\text{C}$ in nitrogen atmosphere. Thermal curves obtained for most of the compounds were similar in character. All complexes decompose in a single stage and all of them start to lose mass only at around 240 $^{\circ}\text{C}$, indicating the thermal stability of the complex. The stability is due to the strong coordination of the tetradentate ligand with Ln(III) salt resulting in the formation of complex. The TG/DTG plot for the thermal decomposition in air is shown in figure. Single stage decomposition corresponds to the loss of three coordinated ions and ligand molecule resulting in the formation of metal oxide. The final mass data obtained from TG measurement and the theoretical value confirms the final residue as Ln_2O_3 .

Antimicrobial activity

The ligand LH_2 and some of their corresponding metal complexes were screened *in vitro* for their antibacterial activity against two Gram-negative (*Escherichia coli* and *Salmonella typhimurium*) and two Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacterial strains using agarwell diffusion method using Imipenem as standard. The antifungal activity of the ligands LH_2 and some of their complexes were evaluated by agar diffusion method against the fungi *Candida Albicans* and *F.Oxysporium* using Fluconazole as standard. The results of antibacterial and antifungal studies are presented in Table 4 and 5. A comparative study of the ligand and their metal complexes indicates that most of the metal complexes exhibit higher antimicrobial activity than that of the free ligand and the control. Hence complexation increases antimicrobial activity [10,14]. The enhanced activity of the complexes can be explained on the basis of Overtone's concept [15] and Tweedy's Chelation theory [16].

**Table.3 : Results of antibacterial assay (concentration used 1mg/mL of DMSO).
<10: weak, Between 10 and 16: Moderate, >16: Significant**

Compound	Gram-bacteria		Gram-positive	
	<i>E.coli</i>	<i>S.typhi</i>	<i>B.subtilis</i>	<i>S.aureus</i>
LH_2	11	14	13	12
$[\text{Gd}(\text{LH}_2)(\text{NO}_3)_3]$	18	16	08	13
$[\text{Dy}(\text{LH}_2)(\text{NO}_3)_3]$	14	18	17	17
$[\text{Sm}(\text{LH}_2)(\text{NO}_3)_3]$	20	19	18	20
$[\text{Gd}(\text{LH}_2)(\text{NCS})_3]$	22	21	19	19
$[\text{Dy}(\text{LH}_2)(\text{NCS})_3]$	12	18	17	15
$[\text{Sm}(\text{LH}_2)(\text{NCS})_3]$	25	24	21	22
SD*	32	28	31	33

*SD: standard drug-Imipenem

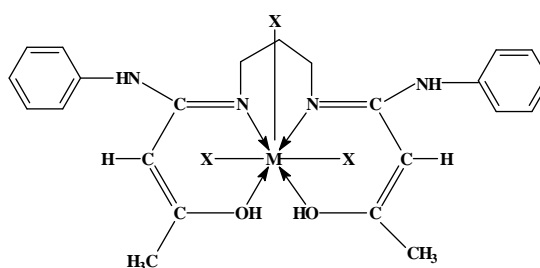
Table .4: Results of antifungal assay (concentration used 1mg/mL of DMSO). <10: weak, Between 10 and 16: Moderate, >16: Significant

Compound	C.albicans	F. oxysporium
LH ₂	16	10
[Gd(LH ₂)(NO ₃) ₃]	19	18
[Dy(LH ₂)(NO ₃) ₃]	24	20
[Sm(LH ₂)(NO ₃) ₃]	18	20
[Gd(LH ₂)(NCS) ₃]	16	19
[Dy(LH ₂)(NCS) ₃]	22	25
[Sm(LH ₂)(NCS) ₃]	20	18
SD*	28	32

SD*: Standard Flucanazole

Conclusion

Analytical data show that all the complexes have the composition $[M(LH_2)(X)_3]$, where M = Sm(III), Gd(III), Dy(III) and X = Cl⁻, NO₃⁻ and NCS⁻. The molar conductance values in DMF and DMSO and the infrared spectral values show that all the complexes are non-electrolytes. Hence all the three ionic groups are present inside the coordination sphere. In the nitrate and thiocyanato complexes the anion is coordinated through nitrogen atom. The thermogravimetric studies reveal the absence of coordinated water molecules. Infrared spectra of complexes reveal that LH₂ behaves as a neutral tetradentate ligand coordinating through two azomethine nitrogen and two enolic oxygen atoms. The infrared spectrum of the nitrate complexes further attests the monodentate coordination of the nitrate group. The magnetic moment values suggest the complexes are paramagnetic. The XRD pattern displayed only a few reflections which cannot be indexed to any crystal system. This indicates the amorphous nature of the metal complexes. A coordination number of seven may be assigned to the metal ion in all the complexes. The tentative structure of the complexes is represented in the Figure 1.

**Figure1. Proposed structure for the complexes**

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