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Synthesis, spectroscopic, characterization and thermal studies of Nd(III), Sm(III) and Gd(III) metal complexes of Tetradentate Schiff Base Ligand

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Abstract

The solid complexes of Nd(III), Sm(III) and Gd(III) with 4-Hydroxy-3-(1-{2-[(2-hydroxybenzylidene)-amino]-4 methyl phenylimino}-ethyl)-6-methyl-pyran-2 one (H_2L) derived from 4-methyl-phenylenediamine, 3-acetyl-6-methyl-(2*H*)pyran,2,4(3*H*)-dione (dehydroacetic acid or DHA) and salicylic aldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-visible, IR,^{1}H-NMR spectra, X-ray diffraction, thermal analysis and screened for antimicrobial activity. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donar atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). The physico-chemical data suggests distorted octahedral geometry for Nd(III), Sm(III) and Gd(III) complexes.. Thermal behaviour (TGA/DTA) of the complexes was studied and kinetic parameters were determined by Horowitz-Metzger and Coats-Redfern methods. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. Fungicidal activity against *Aspergillus Niger* and *Trichoderma.*

Keywords: Dehydroacetic acid, Unsymmetrical tetradentate Schiff Base, Rare Earth metal complexes, thermal analysis, Powder X-ray diffraction and Biological activity.

1. Introduction

Tetradentate Schiff bases with N_2O_2 donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry[1-5]. Schiff bases of *o*-phenylenediamine reported to have variety of applications including biological[6], clinical[7] and analytical[8] fields. Many symmetrical tetradentate bis-type Schiff bases of 1, 2-diamines with *o*-hydroxy aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on unsymmetrical

tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes. In particular those derived from aromatic 1, 2 diamines have been under-investigated[9]. It is worthwhile to mention here that unsymmetrical Schiff bases of this type are difficult to obtain and are not easily isolated [10].

One of the oxygen heterocyclic compounds 3-acetyl–6-methyl-2*H*-pyran 2,4(3*H*)-dione (DHA) was reported to be an excellent chelating agent and to possess promising fungicidal, bactericidal, herbicidal and insecticidal activities[11-15]. It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring system[16]. A search of the literature reveled that no works has been done on Lanthanide(III) nitrate metal complexes of the asymmetrical Schiff base derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde.

2. Experimental

Dehydroacetic acid purchased from Merck was used as supplied. *o*-phenylene diamine and salicylic aldehyde of A.R. grade were used for synthesis of ligand. A.R. grade metal nitrate were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. IR spectra were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ^{1}H-NMR spectra of ligand were measured in $CDCl_3$ using TMS as internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701 respectively. The UV-visible spectra of the complex were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

3. General procedure for the synthesis of ligand

The ligand was prepared by a reported method[16]. A typical procedure for synthesis of Schiff bases was as follows a 50mL solution of 0.10mmol (0.168gm) of dehydroacetic acid, 0.10mmol (0.108gm) of 4 methyl-phenylenediamine and 0.10mmol (0.122gm) of salicylic aldehyde in absolute ethanol was refluxed for about 4hrs. The precipitate thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol (Yield: 87%).(fig. 1)

3.1. General procedure for the synthesis of Metal complexes

To a hot solution of ligand (0.01 mol) in chloroform, methanolic solution (25mL) of metal nitrate (0.01mol) was added under constant stirring. The pH of reaction mixture was adjusted to 7.5-8.5 by adding 10% alcoholic ammonia solution and refluxed for about 6-7hrs. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether (40:60) and dried over calcium chloride in vacuum desiccators (Yield= 55%).

4. Result and Discussion

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in (Table 1). The analytical data of complexes revels 1:1 molar ratio (metal: ligand) and corresponds well with the general formula $[ML(H_2O)_2.NO_3.]$ (where M=Nd(III), Sm(III) and Gd(III). The magnetic susceptibilities of Nd(III), Sm(III) and Gd(III), complexes at room temperature are consistent with distorted octahedral

structure. With two water molecules and one nitrate molecule coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TGA-DTA analysis. The metal chelate solution in DMF shows low conductance and this supports their non-electrolyte nature.

4.1. ^{1}H-NMR *spectra of ligand*

The **^{1}H-NM*R*** spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. δ 2.15 (s, 3H, -CH_3), 2.55 (s, 3H, N=C-CH_3), 5.54 (s, 1H, phenolic OH), 5.84 (s, 1H, Ar-H), 6.90-7.40 (m, 8H, Ar-H), 8.60 (s, 1H, N=C-H), 15-80 (s, 1H, enolic OH of DHA moiety)

4.2. Mass Spectra of the Ligand

Mass Spectra data confirm the structure of the Ligands HL as indicated by the peaks corresponding to their molecular mass

4.3. FTIR. spectra

The IR spectrum of free ligand shows characteristic bands at 3060-3300, 1708, 1620, 1341 and 1253 cm^{-1} assignable to intramolecular hydrogen bonded (υ OH), lactone carbonyl (υ C=O), azomethine (υ C=N), aryl azomethine (υ C-N) and phenolic (υ C-O) stretching modes respectively[17,18]. The data is given in Table 3. The absence of a weak broad band in the 3060-3300 cm^{-1} region, noted in the spectra of the metal complexes indicates deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by upward shift in phenolic (υ C-O)[19] to the extent of 30-50 cm^{-1}. On complexation, the υ (C=N) band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of the azomethine group is coordinated to the metal ion. This is supported by upward shift in υ C-N to the extent of 10-50 $cm.^{-1}$ [20]. The IR spectra of metal chelates showed new bands in the 420-535 cm^{-1} assigned to (M-N)[21-24] and 355-325 cm^{-1} assigned to (M-O) modes [25] . The I.R spectra show a strong band in the 3140-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. Infrared spectra of the nitrato complexes reveled two additional strong bands around 1486 and 1279 cm^{-1}, which were absent in the free ligand.[31]The presence of coordinated water is further confirmed by the appearance of non-ligand band in the 825-835 cm^{-1} region, assignable to the rocking mode of water.[26] The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

4.4. Thermal analysis

The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000°C in nitrogen atmosphere using α-Al_2O_3 as reference. The TG/DSC curve of Gd(III) complex of ligand shows three step decomposition. The initial weight loss in the TG curve, 5.24 % (calcd. 5.72 %) corresponds to loss of two coordinated water molecules. This is supported by an endotherm in DSC (ΔTmin=207.47°C). The first step decomposition is from 190 to 380 °C, with 16.25 % (calcd. 16.01 %) mass loss and a broad exotherm (ΔTmax = 261.80^{0}C) in DSC may be attributed to removal of non coordinated part of ligand. The second step decomposition is from 380 to 580°C with 14.03 % (calcd 13.34 %) mass loss and a broad endotherm (ΔTmax = 358.04°C) in DSC may be attributed to removal of coordinated part of ligand. The third step decomposition

is from 580 to 800°C with 10.02 % (calcd 9.85 %) mass loss corresponds to decomposition of coordinated nitrate part of the complex. The mass of final residue corresponds to stable Gd_2O_3 55.13 % (calcd. 55.06%).

4.5. Kinetic calculations

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation (E_a), frequency factor (log A), entropy of activation ($\Delta S^{\#}$) and free energy change ($\Delta G^{\#}$) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Coats-Redfern integral method[22]. The data is given in Table 2. The results show that the values obtained by two methods are comparable. The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex.[26, 27, 28] $\Delta S^{\#}$ values were negative, which indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

4.6. Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus and Escherichia coli* by paper disc plate method.[26,27]. The compounds were tested at the concentration 0.5 mg·mL^{-1} and 1 mg·mL^{-1} in DMF and compared with known antibiotics *viz* ciproflaxin (*Table* 4). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method[29] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (*Table* 5). From Tables 4 and 5, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes.[26] Such enhanced activity of metal chelates is due to lipophilic nature of the metal ions in complexes.[31] The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents, resulting in interference with the normal cell process.[27]

7. Conclusion

In the light of above discussion we have proposed distorted octahedral geometry for Nd(III), Sm(III) and Gd(III). complexes On the basis of the physicochemical and spectral data discussed above, one can assume that the ligand behave as dibasic, ONNO tetradentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig. 2. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes.

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Table .1. Physical characterization, analytical and molar conductance data of compound

Ligand/Complexes	F. W.	M.P. / Decomp. Temp.^{0}C	Magnetc moment μeff (B.M.)	Molar conduc. Mho $cm^2 mol^{-1}$	Found % (Calculated)			
					C	H	N	M
(HL)	376.42	178	-	-	69.54 (69.60)	4.88 (5.01)	7.50 (7.73)	
$[NdL(H_2O)_2]NO_3$	616.67	>300	3.55	27.44	41.65 (41.80)	3.40 (3.50)	6.70 (6.80)	23.10 (23.90)
$[SmL(H_2O)_2]NO_3$	622.79	>300	1.50	26.30	42.10 (42.40)	3.00 (3.50)	6.60 (6.70)	24.00 (24.40)
$[GdL(H2O)_2]NO_3$	629.68	>300	7.95	27.20	41.70 (41.90)	3.10 (3.50)	6.60 (6.60)	24.00 (24.70)

Table 2. The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CM)

Complex	Step	n	Method	E_a (kJmol^{-1})	Z S^{-1}	ΔS# $JK^{-1}mol^{-1}$	ΔG# (kJmol^{-1})	Corelation coefficient (r)
Nd(III)	I	0.7	HM	7.02	79.65×10^3	154.12	14.93	0.9990 0.9960
			CR	17.12	81.63×10^3	153.92	14.94	
		1.9	HM	26.89	51.61×10^6	157.58	43.35	0.9990 0.9990
			CR	21.54	27.52×10^6	156.73	40.02	
	II	0.7	HM	7.02	79.65×10^3	154.12	14.93	0.9990 0.9960
			CR	17.12	81.63×10^3	153.92	14.94	
		1.9	HM	26.89	51.61×10^6	157.58	43.35	0.9990 0.9990
			CR	21.54	27.52×10^6	156.73	40.02	
	III	0.9	HM	13.00	30.73×10^6	160.73	17.13	0.9870
			CR	14.64	14.58×10^6	145.77	17.67	0.9910
			HM	13.00	30.73×10^6	160.73	17.13	0.9870
			CR	14.64	14.58×10^6	145.77	17.67	0.9910

Table.3 IR Spectra of the ligand (HL) and its Metal complexes (cm^{-1}).

Ligand/Complexes	(OH)	(C=O)	(C=N)	(C-N)	(C-O)	(NO_3)	(NO3)	(M-N)	(M-O)
HL	2625-3346	1708	1621	1340	1252				
$[NdL(H_2O)_2]NO_3$		1685	1603	1371	1294	1485	1270	410	517
$[SmL(H_2O)_2]NO_3$		1671	1603	1380	1262	1480	1272	405	525
$[Gd(H_2O)_2]NO_3$		1654	1597	1383	1281	1484	1278	410	532

Table 4. Antibacterial activity of compounds

Inhibition Zone (mm)				
	E.Coli		*Staphylococcus*	
Ligand/Complexes	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	29	32	31	35
(HL)	11	14	12	15
$[NdL(H_2O)_2]NO_3$	16	20	18	22
$[SmL(H_2O)_2]NO_3$	18	21	19	23
$[GdL(H_2O)_2]NO_3$	21	24	22	25

Table 5. Antifungal activity of compounds Yield of Mycelial dry weight in mg (% inhibition)

Inhibition Zone (mm)				
	Aspergillus Niger		*Trichoderma*	
Ligand/Complexes	500ppm	1000ppm	500ppm	1000ppm
Control	79	79	70	70
(HL)	60(24)	22(72)	38(46)	17(76)
$[NdL(H_2O)_2]NO_3$	44(45)	17(79)	28(60)	11(86)
$[SmL(H_2O)_2]NO_3$	40(50)	16(80)	23(68)	10(88)
$[GdL(H_2O)_2]NO_3$	35(56)	14(83)	18(75)	08(90)

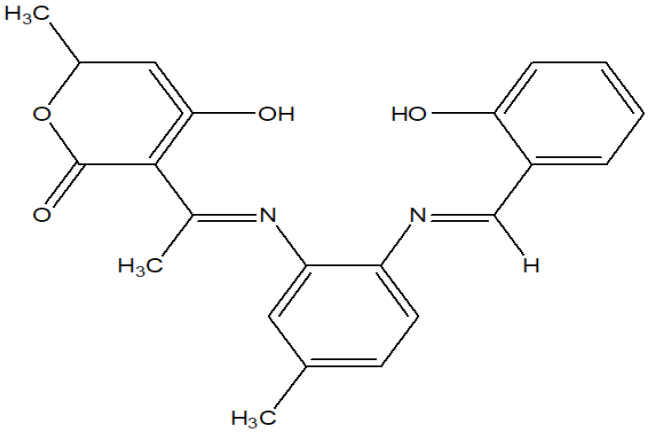


Figure 1. Structure of ligand

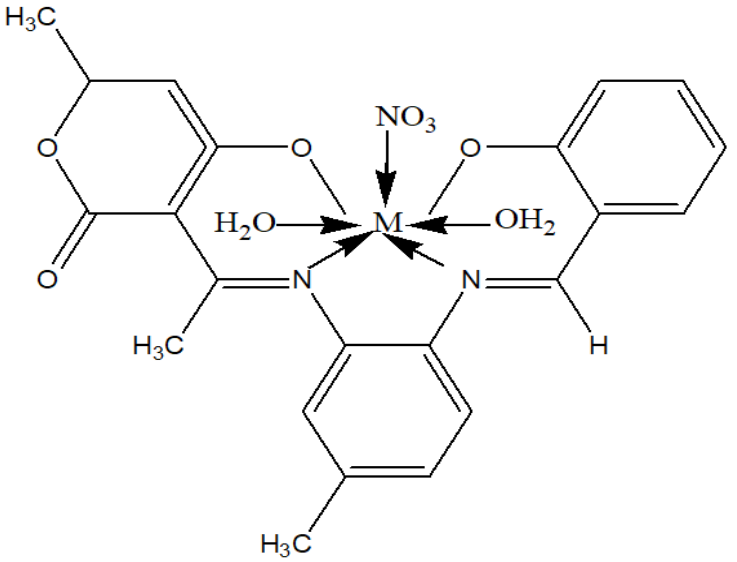


Figure 2. Structure of Metal Complexes

Where M =Nd (III), Sm (III) and Gd

Declaration of Conflicting Interests

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