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SYNTHESIS AND ANTIMICROBIAL STUDY OF METAL COMPLEXES OF SM (III), EU (III) AND ASYMMETRICAL LIGAND DERIVED FROM DEHYDROACETIC ACID

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Keywords:

Tetradentate schiff base, Salicylaldehyde, Powder X-ray diffraction, TGA/DSC spectral analysis and antimicrobial activity

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ABSTRACT: Tetradentate Schiff bases are synthesized from o-phenylenediamine, 5-bromo Salicylaldehyde, and 3-Acetyl-6-methyl-pyran-2, 4-dione, and then its colored complexes of Sm (III) and Eu (III) are formed. The structure of ligand and complexes are characterized by elemental analysis, magnetic susceptibility, thermal analysis, X-ray diffraction, 1H-NMR, mass, IR, UV-visible spectra, and conductometry. TGA/DSC spectral and kinetic parameter of the complexes was studied eagerly. The x-ray diffraction data proposes Tetragonal crystal system for Sm (III) complexes and orthorhombic for Eu (III) complexes. The ligand and their metal complexes were subjected for antibacterial activity against Escherichia coli, *Staphylococcus aureus*, Pseudomonas Aeruginosa using the agar cup-plate method, and antifungal activity was observed by poison plate method against *Aspergillus niger*, *Aspergillus flavus*, *Penicillium chrysogenum*. The results obtained above are in good agreement with previous findings with respect to the comparative activity of the free ligand and its complexes. The result of an investigation of antimicrobial activity indicates that all the ligands show an inhibitory effect against all the pathogens.

INTRODUCTION: In the present investigation, study of various colored complexes of Sm(III), Eu(III) with tetradentate ligands (Schiff Base)were synthesized and characterized. The novel series of lanthanides of tetradentate Schiff bases formed by the reaction of o-phenylenediamine, dehydroacetic Acid (DHA) and 5-bromo salicylaldehyde.

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MATERIALS AND METHODS:

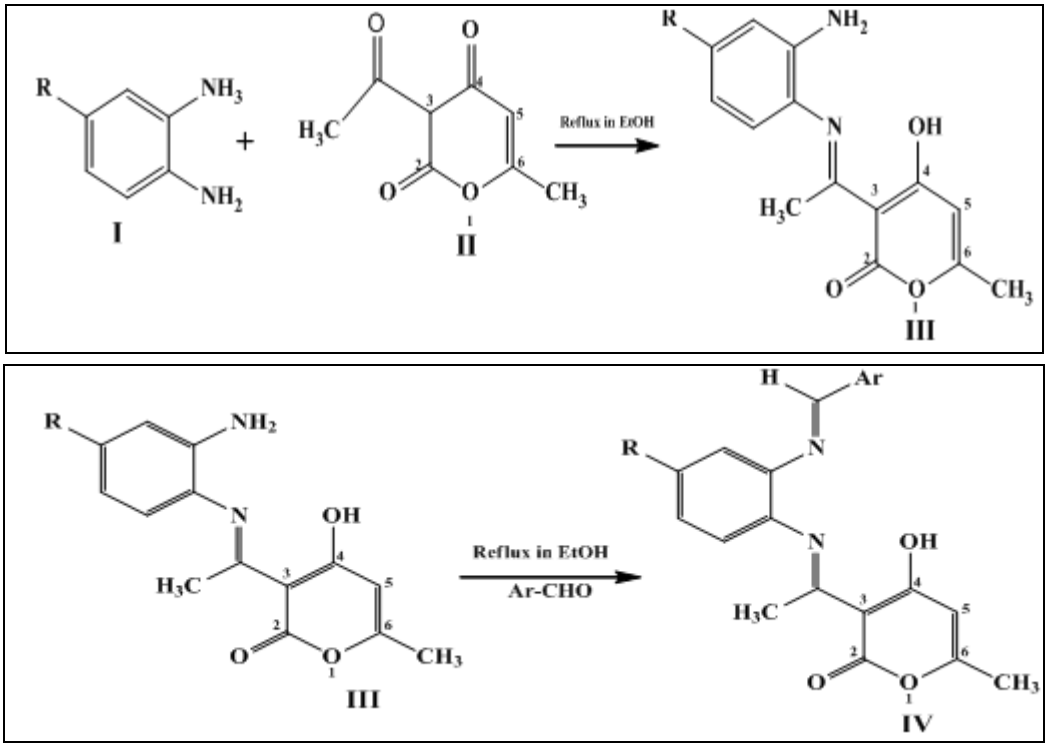
Experiments: The reagents, solvents, DHA, *o*-phenylenediamine and 5-bromo salicylaldehyde of AR grade supplied by Merck were used for the synthesis of ligand. All metal chlorides used for synthesis of complexes are also AR grade.

Instrumentation: ^{1}H-NMR was recorded on FT NMR spectrometer (400 MH_Z) model Advance-II (Bruker) in $CDCl_3$ as a solvent and tetramethylsilane as the internal standard. C, H, N was carried out on Thermo Scientific (FLASH 2000) CHN elemental analyzer. IR study has been carried out on Perkin Elmer-Spectrum RX-I FTIR spectrometer using KBr pellets.

The TGA/DSC and XRD were recorded on TA Inc. SDT-2790 and Pananalytical X'Pert Pro, respectively. All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer.

Molar conductance of complexes was probed on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

Synthesis of Ligand: The synthesis was carried out in two steps; first step is a synthesis of mono-Schiff base, which was prepared by refluxing 50 ml solution of (10 mmol) of DHA and (10m mol) *o*-phenylenediamine in absolute ethanol for about 3 h. The progress of the reaction was monitored with TLC. Thus formed mono-Schiff base then refluxed with 10 mmol of 5-bromo Salicylaldehyde to form tetradentate Schiff base. Obtained solid was then cooled at room temperature and collected by filtration and recrystallization using super dry ethanol (Yield: 76%).



Where R= H / CH_3 and Ar = 5- bromosalicylaldehyde

FIG. 1: SYNTHESIS OF LIGAND

Synthesis of Metal Complexes: A solutions of (1:1) ratio of ligand (0.01mol) and metal chloride (0.01 mol) were prepared in methanol and mixed in hot conditions with continuous stirring to form metal complexes. The mixture was refluxed for 3-4 h. Heat on water bath till the volume of the reaction mixture is reduced to half. After cooling solid metal complex is appeared. Obtained solid metal complex was purified by petroleum ether and dried over vacuum desiccator (yield: 78%).

RESULTS AND DISCUSSION: Physical characterization, analytical and molar conductance data of compounds are given in **Table 1**. From the data it was analysis that, equimolar stoichiometry (metal: ligand) is formed and it also satisfying general formula as ML $(H_2O)_2$ (where M =, Sm (III), Eu(III).

The study of magnetic properties indicates octahedral geometry for Sm(III), Eu (III) at room temperature and two water molecules are coordinated to the metal ion.

Existence of two coordinated water molecules was further confirmed by weight loss before 270 °C in TGA-DSC analysis.

^{1}H-NMR Spectra of Ligand: From ^{1}H NMR spectral data it shows the following signals 2.07 δ (s, 3H, C_6-CH_3), 2.13 δ (s, 3H, N=C-CH_3), 5.83 δ (s, 1H, C_5-H), 6.73-7.04 δ (m, aromatic protons), 8.96 δ (s, 1H, N=C-H),9.98 (phenolic (-OH)

hydrogen of phenyl ring) and 15.89 δ (s, 1H, enolic OH of DHA moiety) [1, 2, 3].

IR Spectra: The IR data of ligand (H_2L) and its metal complexes are listed in Table 2. It depicts prominent bands at 3360, 1685, 1660, 1353, and 1230 cm^{-1} assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), υ C-N (aryl azomethine) and υ C-O (phenolic) stretching modes respectively [4]. The presence of a strong, broadband in the 3360 cm^{-1} regions in the spectra of the ligand, which is not observed in complexes, elucidates coordination of phenolic oxygen to the metal ion by deprotonation [5].

Resulting upswing to an extent of 40-60 cm^{-1} in the υ C-O (phenolic) band [6]. This shift further confirms the involvement of the enolic oxygen in C-O-M bond. Chelation by nitrogen of azomethine (C=N) is confirmed by observing band at 1660 cm^{-1} in the spectra of ligand, which find at lower frequency 1612-1556 cm^{-1}whencomplex formed [7].

This change can be supported by transfer of electrons from nitrogen to the vacant d-orbitals of the metal. Finding new bands in the 521-525 and 461-477 cm^{-1} regions confirms the M-O and M-N bonding, respectively [8]. No any change in skeletal vibrations (C=C) upon complexation. The presence of coordinated water is confirmed by the appearance of a strong band in the 3363-3416 cm^{-1} region in case of Sm(III) and Eu(III)which is also supported by the appearance of a non-ligand band in 825-846 cm^{-1} region, quoted for a rocking mode of water [9].

Magnetic Susceptibility and Electronic Absorption Spectra: The electronic absorption spectrum of Sm (III) complex contains three bands at 24700, 24000 and 21505 cm^{-1} assignable to the transitions $^6H_{5/2} \rightarrow {}^2P_{9/2,}$ $^6H_{5/2} \rightarrow {}^2P_{5/2}$ and $^6H_{5/2} \rightarrow {}^3P_{13/2}$ charge transfer respectively. The electronic absorption spectra of Eu(III) complex show three strong bands at 17500, 24500, and 27800 cm^{-1} which may be assigned to the transitions $^8S_{7/2} \rightarrow {}^6P_{5/2}$, $^8S_{7/2} \rightarrow {}^4P_{7/2,}$ and charge transfer, respectively. Electronic transitions together with magnetic moment value 1.50 B.M. of Sm(III) complex and 7.92 B.M. for Eu(III) complex suggest high spin octahedral geometry for complex [10, 11].

TABLE 1: PHYSICAL CHARACTERIZATION, ANALYTICAL AND MOLAR CONDUCTANCE DATA OF COMPOUNDS

Compound Molecular formula	Mol. Wt.	M.P / Decomp Temp. °C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated) C	H	N	M
(H_2L)	433.50	189	Dark		69.23	6.24	9.67	
$C_{25}H_{27}N_3O_4$			Saffron	----	(69.27)	(6.28)	(9.69)	-----
[$LSm(H_2O)_2$]	617.87	286	Dark	26.21	48.60	4.73	6.80	24.34
			Brown		(48.55)	(4.69)	(6,76)	(24.30)
[L $Eu(H_2O)_2$]	619.48	285	Dark	23.10	48.47	4.70	6.78	24.53
			Brown		(48.40)	(4.65)	(6.72)	(24.49)

TABLE 2: IR DATA OF LIGAND AND METAL COMPLEXES

Compound	IR band frequency (cm^{-1})							
	ν(OH)	*ν*(C=O)	*ν*(C=N)	C=C	C-N	C-O	M-O	M-N
L	3360	1685	1660	1519	1353	1230	-	-
Sm-L	3363	1655	1612	1556	1384	1256	521	461
Eu-L	3416	1654	1595	1571	1399	1250	525	477

Thermal Analysis: The TG/DSC analysis of Sm (III) and Eu (III) complexes was done from ambient temperature to 1000°C in a nitrogen atmosphere using α-Al_2O_3 as reference. In the TG curve of Sm (III) complex, the first weight loss 6.834 % occurred at a temperature between 150-200°C indicating coordinated water in these complexes supported by an endotherm at ΔT_{min} = 214. 22°C. The second step slowed decomposition from 200-600 °C with a mass loss 29.83%. This can be further confirmed by observing broad exothermic peak in DSC with $\Delta T_{max.}$ = 373. 61°C indicates to the removal of the coordinated part of ligand [12, 13]. The TG-DSC curve of Eu (III) complex show first mass loss 6.893% begins between the range 150-250°C and an endothermic peak in this region ΔT_{min} = 313.71°C, indicating loss of two coordinated water molecules. The

second step slowed decomposition from 250-600 °C with 27.99% mass loss (calcd. 26.32%). This can be further confirmed by observing exothermic peaks in DSC with ΔT_{max}. = 397.97°C indicates decomposition of non-coordinated part of ligand. The second slow step from 600-800°C with mass loss 18% corresponds to the removal of the coordinated part of the ligand. A broad endotherm in DSC is observed for this step [14].

Kinetic Calculations: The kinetic and thermodynamic parameters *viz* ΔG (free energy change), ΔS, z (pre-exponential factor), E_a, and n (order of reaction), together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method and Coats-Redfern integral method The data is arranged in **Table 3**. The results show that the values obtained by the two methods are analogous.

Low Ea values of the complexes indicate the autocatalytic effect of metal ion after thermal decomposition [15, 16].

TABLE 3: THE KINETIC PARAMETER OF METAL COMPLEXES CALCULATED BY THE METHODS HOROWITZ-METZGER (HM) AND COATS-REDFERN (CR)

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient (r)
	I	1.80	HM	40.18	14492	-155.10	48.39	0.9998
Sm(III)			CR	38.98	172113	-152.85	44.98	0.9985
	II	1.20	HM	60.58	83114	-150.34	78.74	0.9993
			CR	55.00	362280	-157.15	48.47	0.9984
	I	1.18	HM	47.55	15365	-135.23	55.45	0.9984
Eu(III)			CR	32.55	47183215	-128.45	45.89	0.9989
	II	1.20	HM	28.20	85456	-154.96	40.54	0.9989
			CR	36.98	35088264	-145.62	49.65	0.9987

Ea in kJ mol-1, Z in S-1, ΔS in JK-1mol-1and ΔG in kJ mol

Powder X-ray Diffraction: Scanning of x-ray diffract gram of Sm(III), Eu (III), and metal complexes of L is done at wavelength 1.543 Å in the range 5-100°. The x-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using the computer program [17]. The diffract gram of Sm(III) complex of L had ten reflections with maxima at 2θ = 21.356°, corresponding to d value of 3.93521Å.The unit cell of Sm(III) complex of L yielded values of lattice constants, a=9.26993 Å, b= 9.22178 Å, c = 7.71860 Å and unit cell volume V=470.6505(Å) ^{3} [18]. The diffract gram of Eu(III) complex of L shows eleven reflections with maxima at 2θ = 17.256° corresponding to d value 5.47562 Å. The unit cell of Eu(III) complex of L yielded values of lattice constants, a=18.264632 Å, b=8.18910Å, c = 5.983770Å and unit cell volume V=532.72466(Å) ^{3}. In respect of these cell parameters, the condition such as a ≠ b ≠ c and α = γ = β = 90° required for sample to be tetragonal were tested and found to be satisfactory in Sm(III) complex. While a ≠ b ≠ c and α = β= γ = 90° for sample to be orthorhombic were tested and found to be satisfactory for Eu (III). Density values of the complexes were determined practically using a specific gravity method and found to be 1.9706, 2.9800gcm-3 for Sm(III) and Eu (III) complexes, respectively. Theoretical density was found to be 1.98241, 2.8582 gcm-3 for respective complexes and found near experimental value. By using experimental density values, the molecular weight of complexes, Avogadro's number and volume of the unit cell were computed [19].

Antimicrobial Activity: Ligand and metal complexes are subjected for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus, Pseudomonas aeruginosa* by Agar Cup Method [20, 21]. The compounds were tested at the concentration of 1% in DMSO and Ciproflaxin as standard **Table 4**. For fungicidal activity Poison plate method is used, compounds were tested against *Aspergillus niger, Aspergillus flavus, Penicillium chrysogenum*. Potato Dextrose Agar is used as a medium, and depicted in **Table 5** by comparison with Griseofulvin as standard. Observing **Table 4** and **5**, the conclusion made that the inhibition by metal complexes is more than a ligand. Solubility of metal complexes in organic solvents increases its activity. Hydrogen bonding with the active center of cell may be responsible for enhanced activity [22].

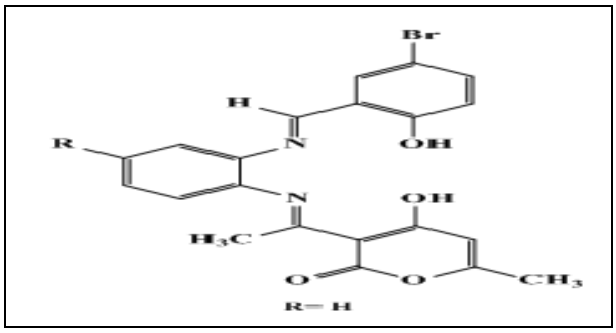
TABLE 4: ANTIBACTERIAL ACTIVITY OF COMPOUNDS

Test Compound	Diameter of inhibition zone (mm)		
	E. coli	***S. aureus***	***Ps. aeruginosa***
Ciprofloxacin	25	50	25
L	09	10	11
L-Sm	12	14	15
L-Eu	13	13	14

TABLE 5: ANTIFUNGAL SCREENING OF LIGAND AND THEIR METAL COMPLEXES

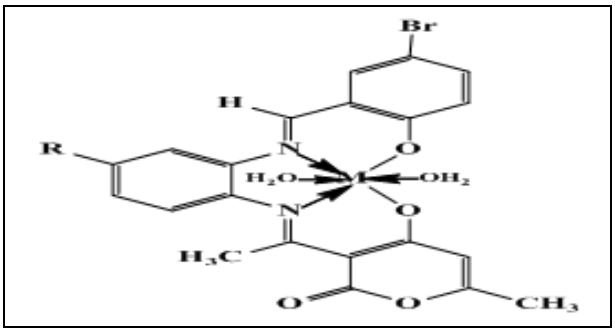
Test Compound	Microorganisms		
	Asp. niger	***Asp. flavus***	***Pen. chrysogenum***
L	-ve	-ve	-ve
L-Sm	RG	-ve	-ve
L-Eu	-ve	+ve	-ve
DMSO	+ve	+ve	+ve
Griseofulvin	-ve	-ve	-ve

-ve -No growth Antifungal activity present , +ve -Growth Antifungal activity absent RG -Reduced growth.



M=Sm (III)

FIG. 2: THE STRUCTURE OF THE LIGAND



Eu (III)

FIG. 3: PROPOSED STRUCTURE OF THE COMPLEXES

CONCLUSION: In the present investigation tetradentated ligand of Schiff Base and its transition metal complexes of Sm(III) and Eu (III) was synthesized. Spectral analysis studies suggest that azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions **Fig. 1**.

Proposing octahedral geometry for Sm (III) and Eu (III) complexes also concluded that the ligand is dibasic and ONNO tetra dentate metal complexes. A study of Microbial activity shows that complexes have enhanced antimicrobial activities as compared to their free ligand. The x-ray diffraction data proposes Tetragonal crystal system for Sm (III) complexes and orthorhombic for Eu (III) complexes. From Thermal data, it predicts the thermal behavior of complexes.

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CONFLICTS OF INTEREST: The author declares that there are no conflicts of interest in submitting this manuscript.

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