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Synthesis and characterization of lanthanide complex derived from tetradentate schiff base and it's antimicrobial activity

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ABSTRACT

New metal complex of La(III) ion with a tetradentate Schiff base derived from salicylaldehyde and ethylenediamine have been investigated. The obtained C, H and N elemental analysis data showed the formation of 1:1 [M:L] ratio. The prepared complex revealed a electrolytic nature. The magnetic moment value of the complex exhibited the existence of diamagnetic phenomena. The coordination behavior of the metal ion towards to the investigated Schiff base takes place through –C=N and –OH groups. The electronic spectral data of the complex displayed the proper transitions and the expected geometrical structure. La(III) complex showed the presence of an octahedral structure and is supported by the data which obtained from the electronic transitions. The salen schiff base was studied for antimicrobial activities against Gram positive (E.Coli and staphylococcus aureus) and Gram negative (Aspergillus niger and Alternaria). The complex exhibited a variable activity of inhibition on the growth of the bacteria.

Key words: Salen, La(III) complex, salicylaldehyde, ethylenediamine, antimicrobial activity

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INTRODUCTION

Salen-based complexes are a fundamental class of compounds in coordination chemistry, and they have been known since 1933 [1]. Interest in these complexes intensified in 1990 when the groups of Jacobsen [2] and Katsuki [3] discovered the enantioselective epoxidation of unfunctionalized alkenes using chiral Mn (salen) complexes as catalysts. Since then, an extremely wide variety of reactions catalyzed by salen complexes has been investigated. These include epoxidation of alkene [4], hydrolytic kinetic resolution of epoxides [5], intermolecular hydroamination of allenes [6], and vinyl polymerization of norbornene [7]. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications [8-9].

In the area of the bioinorganic chemistry, interest in the Schiff base complexes with transition and inner-transition metals has centred on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and enzymes [10-12]. They appear to be of importance for a broad range of transition metal catalyzed reactions including lactide polymerization [13-14], epoxidation of olefins [15] and hydroxylation [16]. Several reviews have been published on metal Schiff bases especially on metal Salen Schiff base complexes [17-18] Salen ligands bind metal ions through four atoms, two nitrogen and two oxygen atoms.

The main aim of the present paper is to prepare a symmetrical Schiff base ligand (derived from the reaction of salicylaldehyde and ethylenediamine) and its complex with La(III) ion and illustrate its geometrical structure by using different physical techniques**.** Review of literature did not reveal synthesis and characterization to explore the coordination chemistry of inner transition metal complex with N,N'-Bis salicylidene ethylenediamine Schiff base

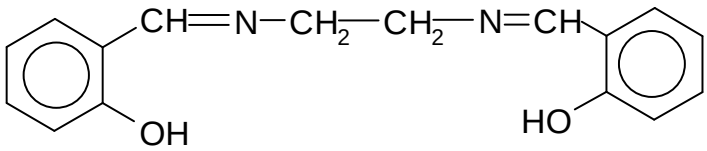
ligand. This has prompted us to synthesize and structural studies of metal complex involving this newly synthesized ligand. This compound N,N'-Bissalicylidene ethylene diamine here after refered to as salen is a ligand having two phenolic –OH and two azomethine groups.

MATERIALS AND METHODS

All the chemicals used were of AR/GR grade. Pure sample of N,N'-Bissalicylidene ethylene diamine and Lanthanide chlorides was obtained from Alfa Acer company.

The melting point was recorded by open capillary method. The molar conductivity at room temperature was determined in conductivity water using Elico CM-180 conductometer using 10-3 M solution in dimethyl sulphoxide. The magnetic susceptibility measurements was made by gouys method at room temperature using powedred samples of complex using $Hg[Co(SCN0_4]$ as a calibrant.. The electronic absorption spectra of the complex in DMSO was recorded on a JascoUV-530 spectrophotometer. The infrared spectra of the solid samples in the 400-4000 cm^{-1} were recorded on a Shimdzu FTIR -4100 spectrophotometer using KBr pellets. XRD data of complex was done on Philips 3701 employing Cu K radiation (λ = 1.541 A^0) in the range 20-90^{0}C. Antimicrobial activity done from Microbiology Department Yeshwant College Nanded.

Synthesis of Schiff base salen



Salen Schiff base was synthesized from salicylaldehyde and ethylene diamine. The ligand under investigation was preapared by the condensation of salicyldehyde (0.02 moles) and 0.01 moles of ethelenediamine for 3 hrs in acidic condition in ethanol. Obtained product was filtered and dried in vaccuo.Yield was 90% and product was shiny yellow. It's melting point recorded in range 127-128^{0}C.

Representative procedure of synthesis of salen complexes

The ethanol containing lanthanum chloride (1mmol) was added dropwise to a hot solution of salen ligand (1mmol) with stirring at the room temperature a yellow coloured precipitate was isolated immediately, filtered and washed by ethanol and dried in vacuo. The yield was about 90%.

General characterization

The yellow products were isolated in excellent yields. The elemental analysis and some physical properties for the ligands and their complex listed in table No.1 and 2.Comprise that the found data are in a good agreement with those theoretical ones, and the obtained analytical data indicate the formation of 1 : 1 [M : L] complex.

Table 1. Analytical data of ligand and its metal complex

Compound	Empirical Formula	Formula Wt	Yield(%)	Color	M.P. ^{0}C	M:K ratio
Salen	$C_{16}H_{16}N_2O_2$	268.31	85	Shiny Yellow	127-128	-
La-Salen	$C_{16}H_{22}N_2O_5Cl_3La$	567.56	90	Dark yellow	>300^{0}C	1 : 1

Table 2. Elemental Analysis data of ligand and its metal complex

Compound	M.F.	Elemental Analysis % found (calculated)					
		C	H	N	O	Cl	M
Salen	$C_{16}H_{16}N_2O_2$	71.62	6.01	10.44	11.93	-	-
La-Salen	$C_{16}H_{22}N_2O_5Cl_3La$	33.86	3.91	4.94	14.09	18.74	24.47

RESULTS AND DISCUSSION

FTIR spectroscopy

The IR spectrum of the Schiff base showed a sharp band near 1635 cm^{-1}, which may be due to azomethine linkage [19-21] which was shifted to1640cm^{-1}, high frequencies in the metal complexes, indicating co-ordination of the metal ions through the azomethine linkage [22]. The ligand showed a strong band at 3251 cm^{-1} due to phenolic –OH group [23]. This band was absent in the spectra of La(III) metal complexes, indicating involvement of this group in the formation of the complex and deprotanation [24]. The absorption bands at 3392 cm^{-1}show the presence of

coordinated water in the complex [25]. The weak band observed at 1247, 1244cm^{-1} characteristics of νC–O (phenolic) [26] in the Schiff base and the metal complex, respectively.

The appearance of the M – N band at 418, cm^{-1} and the M–O band at 530 in the complexe indicate that salen coordinated through an N and a O atom to metal ion [27-28]. The IR spectral data and their tentative assignments are given in Table 3.

Table 3. FTIR spectroscopy data of the ligand and its metal complex

Compound	ν OH	ν C – O	ν C = N	ν M – N	ν M – O	ν H_2O
Ligand	3251	1247	1635	-	-	-
La-Salen	-	1244	1640	418	530	3392

Electronic spectra

The ultraviolet region band shift and intensity alternation of ligand indicates involvement of ligand in the chelation with metal ion [29-30]. The ligand salen shows strong band at 316,262 nm. In case of La(III)-salen complex the strong band observed at 410,317,264 nm. This shifting in the value of band alternation indicates the involvement of ligand in chelate formation.Salen complex is diamagnetic and electrolytic in nature. All the data confirms the octahedral geometry for complex.

Table 4. Electronic Spectral Data of ligand and its metal complex

Complex	Absorbance	ν / cm^{-1}	Assignment	Molar Conductance	Magnetic Moment	Geometry
Ligand	316 262	31645 38167	n π–π*	–	–	–
La -Salen	410 317 264	24390 31645 38167	π–π* (C=N) CT	70	Diamagnetic (–)	Octahedral

Powder X-ray diffraction analysis

-Powder XRD patterns of the selected complexes recorded in the 2θ range from 10 to 90^0 at a wavelength 1.5407 A^0 using Cukα radiation source. Miller indices and interplanar distances are then determined by indexing major diffractograms, lattice parameter a,b,c and α,β,γ are computed from programme and unit cell volume as well as percent porosity calculated from standard formulae. Results of XRD analysis of metal complexes with ligand SEDA results in monoclinic test for lanthanum.

Table.5: Millar indices and interplanar distances of [La(SEDA) Cl_2]2H_2O.Cl complex

h	k	l	2θ(obs)	2θ(calc)	d(obs)	d(cal)
1	1	1	13.71515	13.70638	3.24904	3.25116
-2	0	0	15.51172	15.50532	2.88045	2.88167
-2	1	1	17.24443	17.28348	2.59855	2.59290
0	1	2	19.69050	19.69086	2.28628	2.28628
1	1	2	22.44978	22.44055	2.01726	2.01808
-2	6	0	26.77415	26.76685	1.71007	1.71052
0	6	2	29.41779	29.41725	1.56837	1.56841
3	4	1	31.18293	31.18508	1.48780	1.48772
-2	7	2	35.13687	35.15367	1.33849	1.33794
-2	8	2	38.45175	38.42482	1.23878	1.23953
3	6	2	41.85035	41.84151	1.15462	1.15482
-2	3	4	44.23084	44.23064	1.10436	1.10437
-2	10	2	46.01858	46.00903	1.07057	1.01075
3	11	0	50.91573	50.90381	0.99243	0.99261
4	9	1	52.96300	52.98225	0.96505	0.96481
-1	13	1	54.00721	54.02031	0.95211	0.95196
3	3	4	57.98758	57.99207	0.90850	0.90846
-5	2	4	60.47724	60.50686	0.88529	0.88504
-6	3	3	63.06091	63.03687	0.86411	0.86430
-3	5	5	65.76554	65.75830	0.84480	0.84485
4	12	1	68.64240	68.64538	0.82715	0.82714

Lanthanum complex (fig.) shows maximum reflection at 29^0 of 2θ value with 'd' equal to 1.56837A^0 and lattice type P. Crystal lattice parameters a = 5.8421, b=12.7477 and c=4.7098 A^0. While α=90^0, β=99.3, and γ=90^0, unit cell volume and percent porosity are found to be 350.75cm^3 and 8.536 (table.5) respectively.

[La(SEDA) Cl_2]$2H_2O.Cl$
Crystal system: Monoclinic Lattice Type: P
Lattice Parameter: a= 5.8421 b= 12.7477 c= 4.7098A^0
Lattice Parameter: Alpha= 90 Beta= 99.3024 Gama=90.00^0
Unit cell Volume 350.75 cm^3, % Porosity 8.536

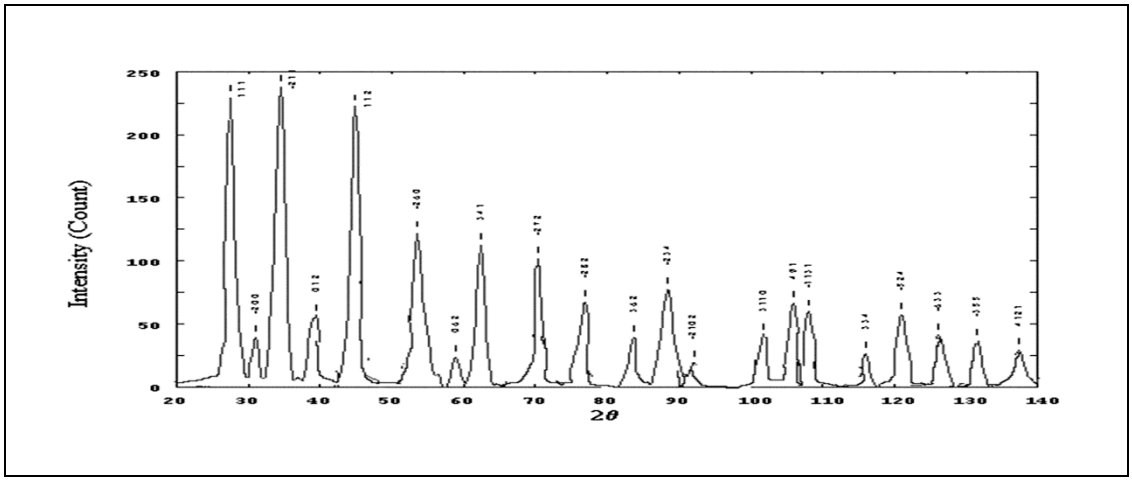


Figure 5: XRD pattern of complex [La(SEDA) Cl_2]$2H_2O.Cl$

Antimicrobial activity
Above synthesized complex and the ligand have been screened against bacteria E.coli and staphylococcus aureus and fungi aspergillus Niger and alternaria. Nutrient agar as medium used for bacteria and potato dextrose agar used for fungi. Incubation of plates with complex solution and ligand solution in well done for 48 hrs at 27^{0}C temperature.

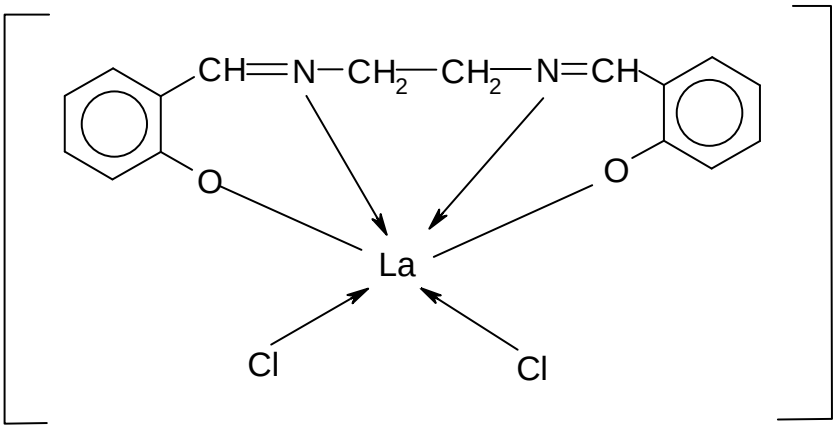
The zone of inhibition based upon size around the well was measured. Inhibition zone percentage is recorded in Table 6 .The percentage inhibition of growth by ligand is less than salen metal complex. Thus complex shows greater activity against micro-organisms as compared to ligand salen. This proves that the chelation increases the antimicrobial activity.

Table 6. Anti-microbial screening data of ligand and La(III) complex

Ligand / Complex	Zone of Inhibition in mm			
	E.Coli	*S.Aureus*	*A.Niger*	*Alternria*
Salen	11	-	-	04
La(III)-Salen	-	09	-	08

CONCLUSION

Hence on the basis of elemental analysis, IR spectra, UV, spectra, magnetic moment data, conductivity measurement and XRD data, following octahedral structure is proposed for La-salen complex



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