

Catalytic and Biochemical Study of Novel Salen Type 2, 2'-(Ethane-1,2-Diylidinitrilo) Bis (Phenylacetic Acid) Complexes of Fe

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ABSTRACT

The salen type complexes of Fe(III) Schiff base were synthesized and characterized by IR spectroscopy, NMR spectroscopy, electronic spectra and thermal analyses. Catalytic study has been carried out for selected redox reactions. Antimicrobial activity of these compound has also been studied.

Keywords: Salen type Complexes, catalytic study, Antimicrobial activity, 2,2'-(ethane- 1,2-diyldinitrilo)bis(phenylacetic acid).

INTRODUCTION:

Salen type complexes, known since 1933, are now the most important stereo chemical models in main group and transition metal coordination chemistry. Metal chelates of salen derivatives have become increasingly valuable as reagents and catalysts of many reactions including electrochemical reduction hydroxylation and Diels-Alder transformation.¹

Salen is a schiff base derived from the condensation of salicylaldehyde and ethylene diamine. It is a symmetrical molecule and exhibits chiral properties. Schiff base are frequently studied due to their biological activity² as well as their optical³ and catalytic activity.⁴

Chiral N, N- bis (salicylidene) ethylene diamine (salen) compounds are very popular ligands because of their easy formation and rich coordination chemistry with a large variety of metal ions that has allowed symmetric reactions.⁵ The incorporation of "Salen" moieties in to macro cyclic structures gives rise to supramolecular interactions and the synthesis of salen compounds bearing Lewis acid or Lewis base activating groups are currently investigated for the development of more active catalysts.⁶ The catalytic activity of salen complexes has been studied in a wide variety of reactions during the last two decades.^{7, 8} Chemical kinetics is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend.⁹ Study of kinetics includes empirical studies of the effect of concentration, temperature and hydrostatic pressure on reactions of various types such as studies may be of practical value in concentration with technical process of more fundamental interest are those kinetic studies of chemical reactions in which the objective is to arrive at a reaction mechanism of even more basic significance.

In the present work, the Schiff base ligand 2,2'-(ethane- 1,2-diyldinitrilo)bis(phenylacetic acid)(eddp) was prepared. The complexes of (eddp) with Fe⁺³ were prepared, characterized and subjected to catalytic and also antimicrobial study.

EXPERIMENTAL

(1) Preparation of Schiff base N, N-bis (1-phenylethylidene) ethane-1, 2-diamine

The synthesis of the Schiff base was carried out by mixing a (0.12 mole) 7.2 gm ethylene diamine and (0.24 mole) 28.8 gm acetophenone and (mole ratio 1:2) in a 500ml round bottom flask, 20ml methanol was added in a mixture. The reaction mixture was refluxed for 1.5 hour. Yellow coloured solution was observed. It was kept overnight and the solid product separated out from solution.

(2) Preparation of ligand 2, 2'-(ethane-1, 2-diylidinitrilo) bis (phenylaceticacid)

The synthesis of ligand was carried out by mixing a (0.03 mole) 6.6gm Schiff base and 13gm potassium dichromate and 27ml distilled water in 500ml round bottom flask. 24gm of H₂SO₄ was added drop wise in reaction mixture within 30 minutes with stirring. The heat of dilution of the acid causes the Schiff base to melt and oxidation take place.^{10, 11} When all the sulphuric acid was consumed, and the temperature of the mixture commences to fall, then a reflux condensor was attached to the flask and heated to gentle boiling for 45 to 60 min. The reaction mixture was cooled and poured in to 50ml distilled water. Green precipitates were observed, filtered and washed with 20ml of distilled water. The precipitates were transferred in a 500ml beaker and 5 percent 25ml H₂SO₄ solution (0.7ml conc. H₂SO₄ + 24.3ml water) was added and digested for 20 minutes on a water bath with agitation in order to remove the chromium salt. The reaction mixture was allowed to cool and filtered again. The precipitates are transferred in a beaker and any lumps of material were broken. Then it was treated with 5 % NaOH solution until the liquid remained alkaline.

The solution was heated about 20 minutes to 35°C to 45°C temperature and filtered. To the filtrate, 5% H₂SO₄ was added drop wise. The precipitates were filtered and dried in oven at 65°C.

(3) The Synthesis of complex (M –EDDPA):-

The synthesis of complex was carried out by mixing 25ml 0.2M metal perchlorate solution and 25ml 0.2M ligand as alcoholic solution. The reaction mixture was refluxed for 2.5 to 3 hours at 90°C temperature. After 3.0 hours the reaction mixture was cooled. There was no immediate precipitation. The pH of the above solution was then raised to 6.0 using 0.1M sodium hydroxide solution which resulted in the precipitation of the solid. The complex thus obtained was washed well with (1:2) mixture of absolute alcohol and water to remove unreacted metal salt and ligand.

Result and Discussion:

Infrared Spectral study:

IR spectral analysis confirms the presence of characteristic groups in the compound. In the ligand bands at ~3400cm⁻¹ is assigned to the ν (O-H) stretching of the carboxylic acid-OH group. The sharp band at 1583cm⁻¹ can be attributed to the ν (C=N) stretching mode in the ligand. This band shifted in the chelates. The band at 1717 cm⁻¹ of the ligand is due to the C=O stretching. In the Fe-Salen, it is shifted to 15-40 cm⁻¹ either lower energy or higher energy indicating the coordination by the carbonyl- oxygen atom.

Further conclusive evidence of this ligand with metal ion was shown by the appearance of weak low frequencies new bands at 550-650 cm⁻¹ and 450-500 cm⁻¹. These were assigned to the metal nitrogen (M-N) and metal oxygen (M-O) vibration respectively, and were observed in the spectra of the metal chelates and not in the spectra of the ligand. Thus, this is the confirmation that the N and O atoms participated in the coordination.

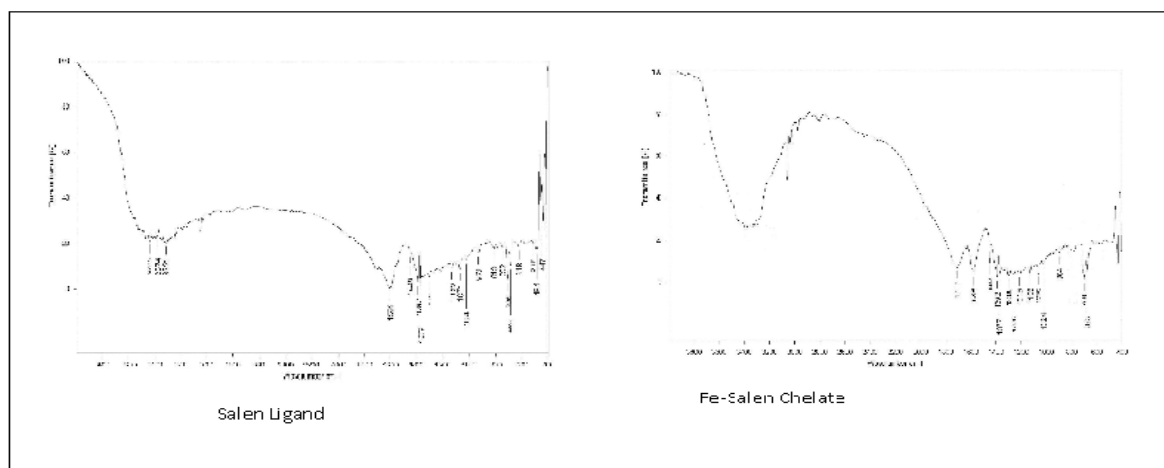


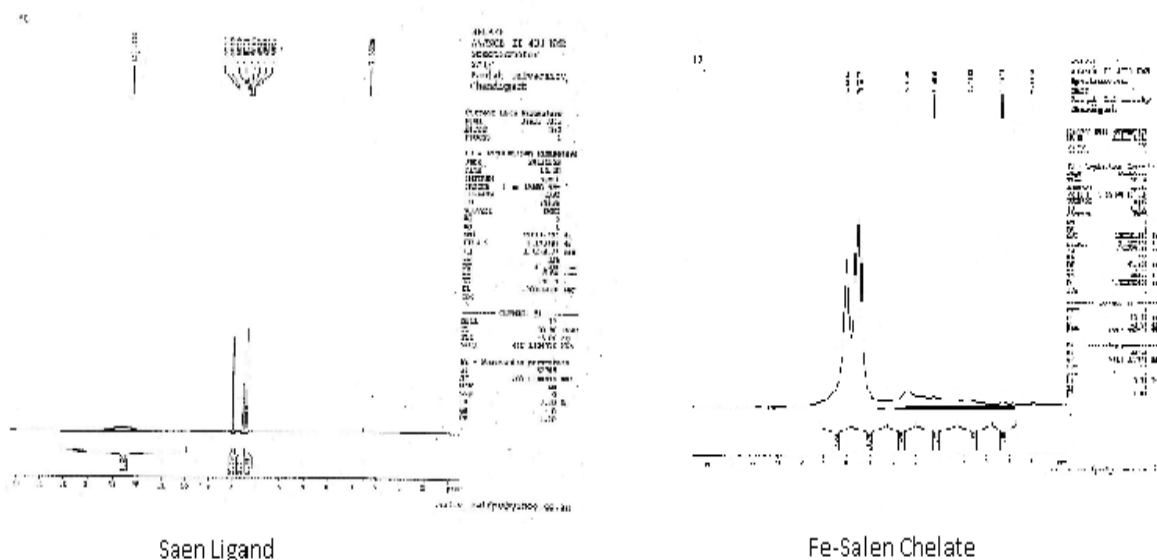
Table -1 Infrared Spectra of the Metal Chelate and ligand (cm⁻¹)

Compound	v(O-H) Str.	v[Ar(C-H)] Str.	v(C=N) Str.	v(C=O) Str.	v(M-N) Str.	v(M-O) Str.
Salen	3400 3390	1070 1024	1583 ----	1717 ----	---- ----	---- ----
Fe-Salen	3442 3374 3321	1106 ---- ----	1449 1392 ----	1740 ---- ----	618 570 ----	484 447 ----

NMR Spectral study:

The aromatic protons in ligand appeared in the range δ 7.43 to δ 8.0 ppm. In the metal chelate, the aromatic proton appeared in the range $\sim \delta$ 7.1 to $\sim \delta$ 8.2 ppm which is shifted to upper field. A broad signal at δ 12.47 ppm was observed due to -COOH proton in ligand.

In the chelates, the disappearance of the carboxylic acid (-COOH) proton confirms the coordination by oxygen to metal ion.



Electronic Spectral study:

The UV- Visible spectra of the metal chelates were measured. The electronic spectra of the Fe-Salen showed three band at 27815cm^{-1} , 29166cm^{-1} and 31343cm^{-1} which may be assigned to ${}^4A_1 \rightarrow {}^4E_1$, ${}^6A_1 \rightarrow {}^4T_1$ and ${}^6A_1 \rightarrow {}^4T_2$ transition respectively and are suggestive of their octahedral geometry around the Fe(III) ion.

Magnetic moments:

The magnetic moments of the chelates were measured by the Gouy’s method. The room temperature magnetic moment of the solid Fe-SIn was found to be 5.69 BM. This indicates five unpaired electrons per Fe(III) ion in octahedral environment.

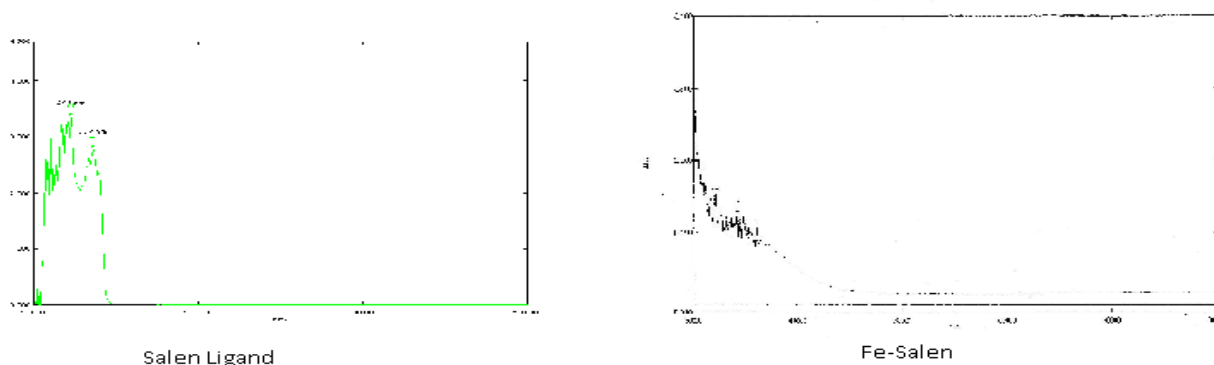


Table-2 Absorption spectral Data and Magnetic Moment of the Metal Chelates.

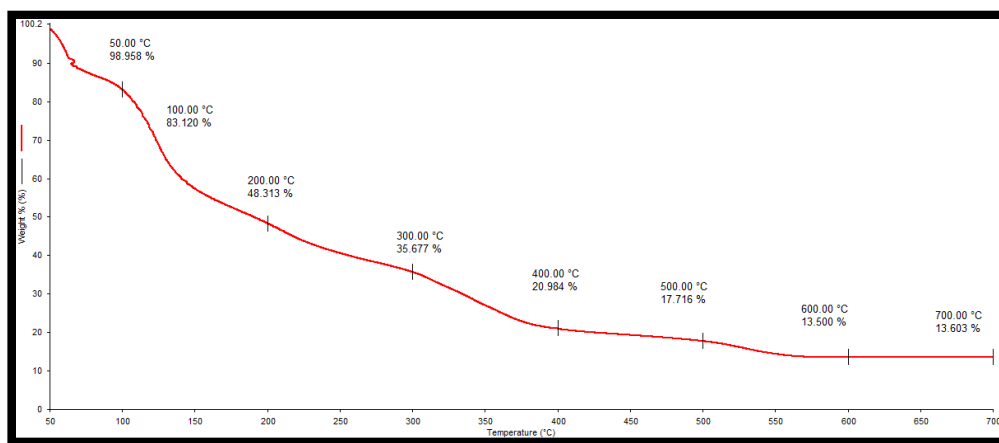
Compound	Transitions		μ_{eff} (B.M.)
	In cm	In nm	
Salen ligand	37037.03	(270)	----
Fe-Salen	27815, 29166, 31343	(359.52), (342.86), (319.05)	5.69

Thermal analysis:-

Thermal analysis of metal complexes is carried out by thermogravimetric analyzer. The heating was carried out until there was no further loss in weight. Change in weight was recorded with time. Thermograms were analyzed by increasing the temperature at uniform rate. The cumulative % weight loss data of metal chelates are shown in table

Table-3 Water Content and Weight Loss Data of the Metal Chelates.

Chelate	RT-100°C			100°C -150°C			150°C-200 °C		
	%	gm	No. of water molecules per chelate molecule	%	Gm	No. of water molecules per chelate molecule	%	Gm	No. of water molecules per chelate molecule
Fe-Salen	16.88	63.78	3H ₂ O	28.74	97.25	5H ₂ O	9.069	34.26	2H ₂ O

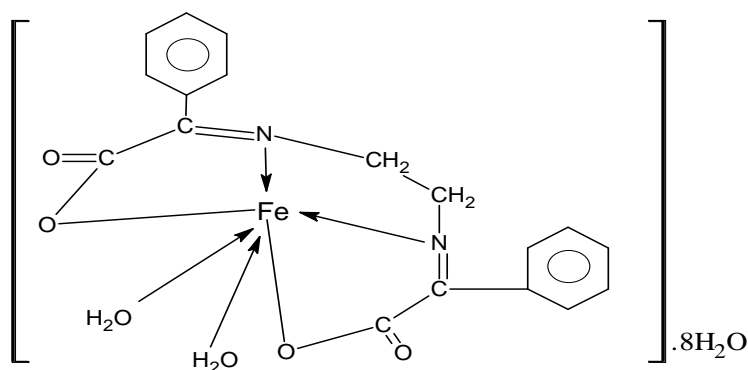


Fe(III) Chelate

It has been observed that Fe-Salen loss in weight two water molecules in range 150⁰C-200⁰C . This indicates that two water molecules coordinate with the Fe-Salen It has been also observed that Fe-Salen, lose weight five water molecules, in range 100⁰C -150⁰C temp. It was observed that at the range of R.T. to 100⁰C temp Fe-Salen lose weight corresponding to four water molecules.

There are eight water molecules that crystallize with Fe-Salen, as water of crystallization or water of hydration.

Based up on all the experimentally data the most probable structures of the metal chelates are shown as below.



Probable structure of Fe-Salen

Catalytic study:

A systematic study of the addition of catalytic amount of newly synthesized chelate was carried out for the redox reactions (1) potassium persulphate (K₂S₂O₈) with potassium iodide (KI), (2) potassium bromate (KBrO₃) with potassium iodide (KI) and (3) hydrogen peroxide (H₂O₂) with potassium iodide (KI). There were six kinetic experiments carried out and six of them were three with the chelate compounds as catalyst and three were without the catalyst. Remaining all other factors were identical. It was observed that addition of all the chelate in catalytic amounts enhanced rate of reaction 4.97%. to 13.0% Fe(III) chelate was able to highest raise the reaction rate of the reaction of BrO₃⁻ + I⁻ in acidic medium. For the remaining two reactions, S₂O₈²⁻ with I⁻ and H₂O₂ with I⁻ in acidic medium, addition of the Fe(III) chelate.

Table-4 Reaction rate of Fe (III) chelate

Reactions	k without chelate	k with Fe-Salen	% Increase in reaction rate at T = 305 K Fe-Salen
$K_2S_2O_8 + KI$	6.7928×10^{-5}	7.1310×10^{-5}	4.97
$KBrO_3 + KI + HCl$	1.5237×10^{-3}	1.7706×10^{-3}	16.20
$H_2O_2 + KI + H_2SO_4$	3.0696×10^{-4}	3.4688×10^{-4}	13.0

Antimicrobial study of chelates of salen ligand

Table-5 Antibacterial Activity of salen ligand and chelates

Antibacterial Activity					
Minimal Inhibition Concentration					
SR. No.	Code No.	<i>E.Coli</i> MTCC 443	<i>P.Aeruginosa</i> MTCC 441	<i>S. Aureus</i> MTCC 96	<i>S.Pyogenus</i> MTCC 442
Microgram /ml					
1	Salen [C ₁₈ H ₁₆ N ₂ O ₄]	100	100	250	500
2	Fe-Salen [Fe(C ₁₈ H ₁₄ N ₂ O ₄).10H ₂ O]	50	50	500	500

The antibacterial activity of the chelates was studied by using four bacterial strains. The antibacterial activity of the ligand also increased when it was chelated with ferric metal ion against *E.Coli* and *P.Aeruginosa*. The antibacterial activity was studied by comparing minimal inhibition concentration (MIC). Five standard antibiotics were selected for comparison with respect to activity against *E. Coli*, *P.Aeruginosa*, *S.Aureus*, *S.Pyogenus*. Fe-Salen was found to be more active than ampicillin against *E.Coli* and *P.Aeruginosa*, and have same activity as chloramphenicol. Against *S.Aureus* and *S. Pyogenus* the Fe-Salen showed less activity compared to the standard antibiotics.

Table-6 Antifungal Activity of salen ligand and chelates:

Antifungal Activity				
Minimal fungicidal Concentration				
SR. No.	Code No.	<i>C. Albicans</i> MTCC 227	<i>A. Niger</i> MTCC 282	<i>A. Clavatus</i> MTCC 1323
Microgram /ml				
1	Salen [C ₁₈ H ₁₆ N ₂ O ₄]	200	500	500
2	Fe-Salen [Fe(C ₁₈ H ₁₄ N ₂ O ₄).10H ₂ O]	500	>1000	>1000

In comparison with the Salen the antifungal activity of Fe-Salen against *C.Albicans*, exhibit similar activity as the standard drug greseofulvin however against *A. Niger* and *A. Clavatus* the antifungal activity of the chelates is less than both the selected antibiotics.

Acknowledgement

The authors are thankful to the Principal, D.N.Science College, Dabhoi and Management of Vadodara Jilla Kelavani Mandal, Dabhoi for providing the necessary laboratory facilities.

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