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Synthesis, characterization and Catalytic study of Novel salen type 2, 2'-(ethane-1, 2-diyldinitrilo)bis(phenylacetic acid) complexes of Zn and Cd

Modh P.H.[1] and Pandya D. R.[2]

[1]*D. N. Science College, Dabhoi*
[2]*Smt. S. S. Patel Nootan Science and Commerce College, Visnagar*

ABSTRACT

The Cd^{II} , Zn^{II}, of salen type complexes of Schiff base were synthesized and characterized by IR spectroscopy, electronic spectra, and thermal analyses. The structure has been assigned based on the above analyses. Catalytic study has been carried out for redox reactions. All complexes are diamagnetic. Antimicrobial activity of these compounds has been measured.

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

INTRODUCTION

Salen type complexes have been known since 1933 and are now the most important stereo chemical models in main group and transition metal coordination chemistry. Metal complexes 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 symmetrical molecule and exhibits chiral properties. Schiff base are frequently studied due to their biological activity[2] as well as their optical[3] and catalytic activity. [4] Chiral N, N^1 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 a 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.[97] Study of kinetics includes empirial 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.

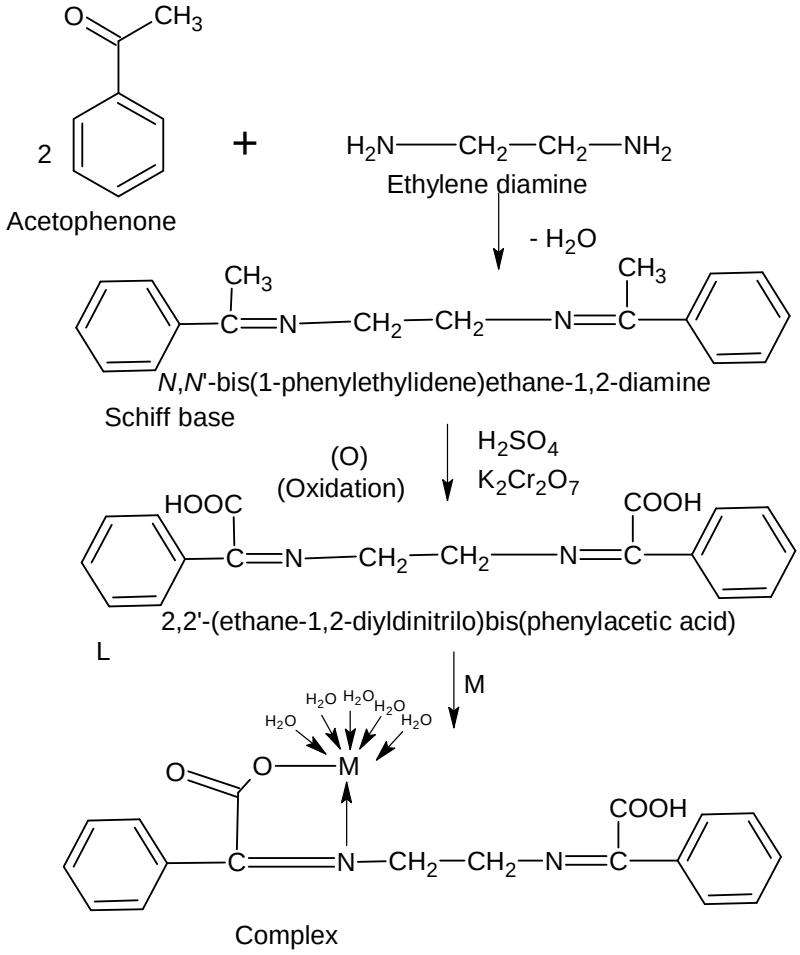
MATERIALS AND METHODS

Experimental

All the chemicals used throughout the course of experimental work were of analytical grade. spectroscopic grade solvents were employed for recording the soectra. Zn(II), Cd(II) perchlorates were prepared.

Preparation of schiff base N,N-bis(1-phenylethylidene)ethane1,2-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 (The mole ratio is 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.



M=Zn and Cd

Preparation of ligand 2, 2'-(ethane-1, 2-diyldinitrilo)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 H_2SO_4 was added dropwise 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, 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 H_2SO_4 solution (0.7ml + 24.3ml water) was added and digested on a water bath with agitation in order to remove the chromium salt for 20 minutes.

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 percent NaOH solution untill the liquid remained alkaline.

Preparation of complex:-
The synthesis of complex was carried out by mixing 25ml 0.2M metal perchlorate solution and 25ml 0.2M ligand alcoholic solution. The mole ratio of ligand and metal was (1:1). 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.

RESULTS AND DISCUSSION

Infrared Spectra study:-
Ligand molecule shows the following characteristic bonds.Mono substituted benzene derivatives of 675 cm^{-1}, 3500cm^{-1} – 3080cm^{-1} (O–H and aromatic =C-H stretching), 1200cm^{-1} C-O stretching, 1590cm^{-1}, 1514cm^{-1} (-C=N stretching). The usual ring skeleton υ C- C and υC-N bands are observed at 1590cm^{-1}, 1500cm^{-1}, 1470cm^{-1}, 1420cm^{-1} and 1525cm^{-1} υC-O and υO-H coupled. 1690cm^{-1}, υ C=O and 3500cm^{-1} – 3080cm^{-1} υ (O-H).In the complex the band around 450cm^{-1} corresponds to υ(M-O) suggest that carboxylic groups are involved in bond formation with metal ions υ(M-N) frequency undergoes coupling with other stretching bands[12]. The bands around 820cm^{-1} and 720cm^{-1} may correspond to the couple M-N vibrations. The presence of M-O-C=O stretching bands in the range 1580cm^{-1} gives a good indication.

Thermal Study
Removal of water molecules at higher temperature in thermo gravimetric analysis indicated to be coordinated to the metal and might be linked to the chelating ketone group thorough hydrogen bonding less the experiment was started by heating the system at a constant rate of 10°C min^{-1}. This would permit recording the loss in weight both as a function of time and temperature. The heating was carried out until there was no further loss in weight. Simultaneously change in weight was recorded with time, when the temperature was increased at uniform rate. The thermo grams were analyzed to obtain information about the percentage weigh-loss at different temperatures. It has been observed that $Zn^{(II)}$ eddpa and $Cd^{(II)}$eddpa show loss in weight corresponding to five and four water molecules in range 100-150°C. It has been observed that at 150°C temperature 93.85gm weight loss occurred. Which indicated that five water molecules coordinated with metal is lost by zinc complex at the said temperature and Cd complex at 150ºC temperature the 77.06gm weight loss occurred. Which indicate that four molecules of water coordinated with metal is lost by cadmium complex at 150ºC temperature[13].

Catalytic study:
A systematic study of the addition of catalytic amount of newly synthesized complexes was carried out for the reactions such as potassium persulphate ($K_2S_2O_8$) with potassium iodide (KI), potassium bromate ($KBrO_3$) with potassium iodide (KI) and hydrogen peroxide (H_2O_2) with potassium iodide (KI).There were nine kinetic experiments carried out and six of them were with the complex compounds as catalyst and three were without the catalyst. Remaining all other factors was identical. It was observed that addition of all the complexes in catalytic amounts enhanced rate of reaction significantly between 8.76% to 94.75%. Which is almost double the original rate? Out of the three reactions selected, Cd complex was able to raise the reaction rate of the reaction of BrO^-_3+I^- in acidic medium around 1.5 times more than corresponding Zn complex. For the remaining two reactions, $S_2O_8^{2-}$ with I^- and H_2O_2 with I^- in acidic medium, addition of the Zn complex increased the reaction rate to a greater extent than addition of Cd complex. Addition of Zn complex resulted in increase of the redox reaction of H_2O_2 and I^- to 1.5 times higher value. Figures indicated that enhancement of the reaction rate of $S_2O_8^-$ and I^- was lowest compared to the enhancement in reaction rate of the other two. The overall increase in reaction rates is most probably due to lowering of activation energy requirement for the selected reactions. It is noteworthy that the formation of salen type structure of Zn or Cd complex is quite efficient to reduce the activation energy requirement of the reaction of $KBrO_3$ and KI.

Table – 1

Compound	Ligand	Zn complex	Cd complex
υ(C-H)	3500cm^{-1}	---	---
υ(C-O)	1100 cm^{-1}	1090 cm^{-1}	1100 cm^{-1}
υ (C=N)	1514 cm^{-1} 1590 cm^{-1}	1500 cm^{-1} 1580 cm^{-1}	1525 cm^{-1} 1590 cm^{-1}
Y(C-O)&(O-H)	1400 cm^{-1} 1420 cm^{-1} 1470 cm^{-1}	1435 cm^{-1} 1470 cm^{-1}	1435 cm^{-1} 1470 cm^{-1}
Y(C=O)	1695 cm^{-1}	1690 cm^{-1}	1700 cm^{-1}
Y(C-H)	2825 cm^{-1}	2830 cm^{-1}	2830 cm^{-1}
υM-N	---	820 cm^{-1}	820 cm^{-1}
Y =C-H	3080 cm^{-1}	3070 cm^{-1}	3090 cm^{-1}

Table – 2 Water content at 25ºC and cumulative weight loss data of the metal complexes at 50ºC, 100ºC, 150ºC

Compound	Found					
	50ºC		100ºC		150ºC	
	Gm	%	gm	%	Gm	%
Zn	0.0	0.0	2.52	0.65	93.85	24.22
Cd	0.0	0.0	5.96	1.37	77.06	17.7

Table – 3Overall Results of Catalytic Activity

Reaction	k without complex	K with Zn eddpa	k with Cd eddpa	Increase in reaction rate at T = 305°C Zn eddpa	Increase in reaction rate at T = 305°C Cd eddpa
$K_2S_2O_8$+ KI	6.9410x10^{-5}	7.7526x10^{-5}	7.5493x10^{-4}	11.69%	8.76%
$KBrO_3$+ KI	1.5088x10^{-3}	2.5274x10^{-3}	2.9385x10^{-3}	67.51%	94.75%
H_2O_2+ KI	3.1056x10^{-4}	4.4720x10^{-4}	3.886x10^{-4}	43.99%	25.12%

Table – 4

compound	color	m.w.	m.p.	RF value	λ max	Magnetic moment
Schiff base	yellow	264	101°C	0.61	_	-
Ligand	white	324	116°C	0.70	200	-
Zn eddpa	white	388	128°C	0.85	227	Dimagnetic
Cd eddpa	white	435	126°C	0.82	227	Dimagnetic

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