Synthesis, Characterization and Microbiological Studies of Zinc(II) Tetraaza Macrocyclic Complexes

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ABSTRACT:

A novel series of tetraaza macrocyclic Zn(II) complexes [$ZnLX_2$] (where L= N_4 donor macrocyclic ligands) and (X= Cl^-, NO_3^- or H_2O) have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, solubility, infrared and ESR.The free Schiff base ligands and their metal complexes were screened for their antimicrobial activity against both Gram-positive and Gram-negative bacteria. It has been found that all the complexes are antimicrobially active and so higher activity than the free ligands. A very strong band around at 1640 cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligands. This was shifted to 1634-1625 cm^{-1} in the complexes, which indicates the coordination of the metal to the azomethine nitrogen. The molar conductivity data of the complexes in DMSO indicate they are non-electrolytes. On the basis of magnetic susceptibility and electronic spectral study, geometry of complexes was proposed to be octahedral.

Keywords: - Benzene-1,2-diamine, pentane-2,4-dione, zinc salt, microbiological activities.

INTRODUCATION:

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first synthesized by Hugo Schiff in 1864. These compounds containing a general formula $RCH = N - R^1$ where R and R^1 are alkyl, aryl, cycloalkyl or heterocyclic groups are also known as anils, imines or azomethines. bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable in general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are less sterically hindered than that of ketones.[1-5] The extra carbon of ketones donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands capable of forming very stable complexes with transition metals.[6-9] They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reaction with a metal ion. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields like biological, inorganic and analytical chemistry. Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity. Schiff bases are widely applicable in analytical determination using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications.[10-12] Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis. Metal containing macrocycles is an interesting field of chemistry with many synthetic and natural macrocyclic compounds investigated.[13-16] The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bio inorganic chemists and is developing very rapidly. Macrocyclic compounds and their derivatives are good hosts for metal anions, neutral molecules and organic cation guests. The metal ion and host-guest chemistry of macrocyclic compounds are very useful in fundamental studies, e.g., in phase transfer catalysis and biological studies. Aza macrocyclic ligands have remained a focus for many decades. The coordination chemistry of macrocyclic complexes is a fascinating area which has attracted the attention of inorganic chemists. The chemistry of metal macrocycles is extensive because of their close relationship to molecules of biological significance. We report here the synthesis, characterization and antimicrobial studies of macrocyclic Schiff base complexes $[Zn(L_1)(H_2O)_2]SO_4$ and $[Zn(L_1) Cl_2]$ obtained from the reaction of the Schiff base ligands(L_1) or (L_2) with the zinc salt.

MATERIALS AND METHODS:

Chemicals and Reagents: - All the reagents such as zinc (II) salts, solvents, pentane-2,4-dione, orthophenylene diamine, DMF, DMSO were purchased commercially and used without any further purification. Suppliers were S Merck, CDH and Aldrich.

Physical Measurements: - The percentage (%) of Zn were determined by EDTA complexometric titration. The elemental analysis of C, H and N was performed by using a Perkin-Elmer 2400 elemental analyzer. The melting point of all compounds were determined using Griffin melting point apparatus. The molar Conductivity were determined by using DMSO as a solvent in digital conductivity meter at 25^0c. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR -8400 spectrophotometer using KBr disc. The magnetic susceptibility was determined on Gouy balance at room temperature using $Hg [Co (SCN)_4]$ as a calibrant. The absorption spectra were recorded by using Shimadzu model UV-1601 spectrophotometer at room temperature in DMF solution.

Synthesis of Schiff base ligand (L_1): -

The Schiff base ligand(L_1) was prepared by adding 1. 0013 g (0.01 mol) of pentane-2,4-dione in 25 ml methanol and 1.081 g (0.01 mol) of benzene-1,2-diamine in 25 ml methanol. The resulting solution was refluxed for 10-12 h. On cooling the reaction mixture, the white crystalline solid was formed. The precipitate is washed with distilled water and methanol several times and is then recrystallized with methanol to obtain the required Schiff base.

Synthesis of Schiff base ligand (L_2): -

The Schiff base ligand(L_2) was prepared by adding 1. 790 g (0.01 mol) of 3-bromopentane-2,4-dione in 25 ml methanol and 1.081 g (0.01 mol) of benzene-1,2-diamine in 25 ml methanol. The resulting solution was refluxed for 16 h. On cooling the reaction mixture, the yellow crystalline solid was formed. The precipitate is washed with distilled water and methanol several times and is then recrystallized with methanol to obtain the required Schiff base.

Synthesis of the metal complexes: -

The metal complexes were prepared by refluxing 0.01 mol of zinc salt with 0.01 mol of Schiff base in methanolic medium for 5-6 h. A little of sodium hydroxide were added in drops to act as catalyst for the reaction. The solution was cooled at room temperature and was stirred for 20 min where by the precipitate of complexes appeared which was filtered on suction and washed with water and then with methanol.

RESULTS AND DISCUSSION:

The analytical data of metal complexes are given in Table 1. The lower values of molar conductance indicate non-electrolytic nature of metal complexes. All metal complexes are coloured and stable in air.

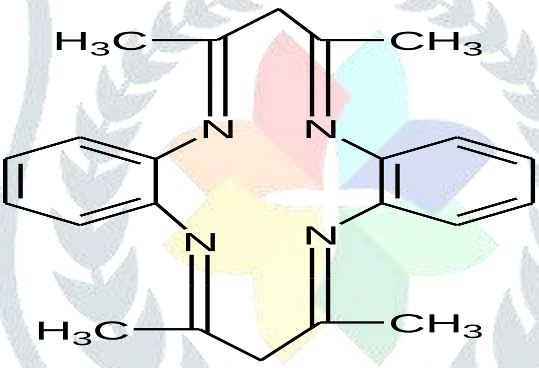

Fig 1. Schiff base ligand (L_1)

($C_{22}H_{24}N_4$)

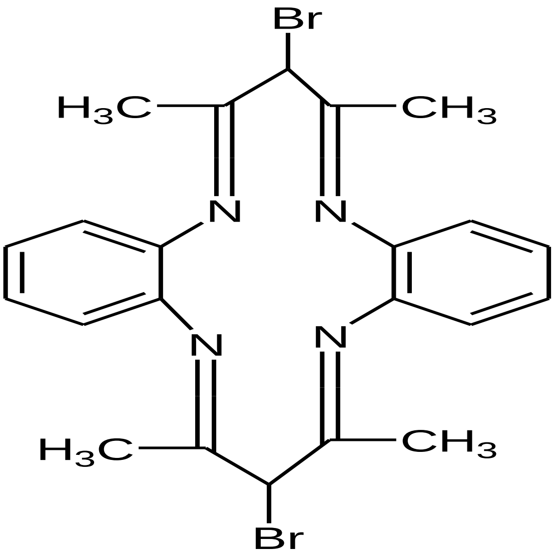

Fig 2. Schiff base ligand (L_2)

($C_{22}H_{22}N_4Br_2$)

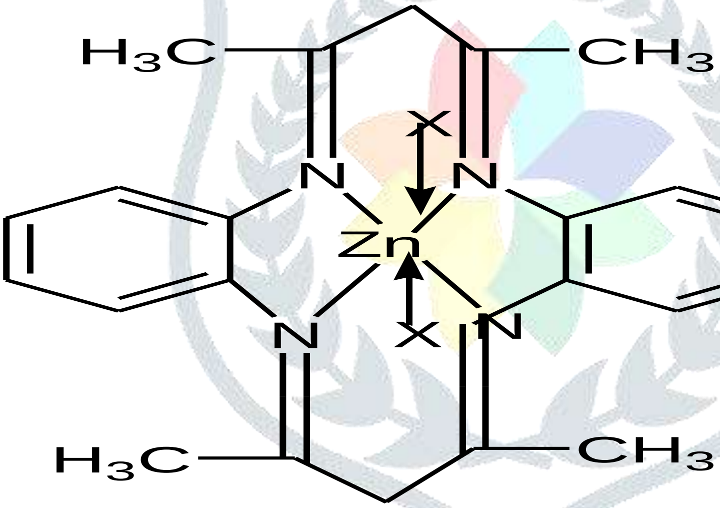

Fig 3. Proposed structure of Zn (II) complexes

(X= Cl, H_20, NO_3^-)

Compounds	color	yield(%)	M.P(^{0}c)	molar conductivity ($S\ cm^2\ mol^{-1}$)
$L_1 = C_{22}H_{24}N_4$	White	82	136	—
$L_2 = C_{22}H_{22}N_4Br_2$	Yellow	72	198	—
$[Zn(L_1)(H_2O)_2]SO_4$	White	77	212	18
$[Zn(L_2)Cl_2]$	Brown	68	280	15

Table: -1 Physical properties of Schiff bases and their metal complexes

. **Table: -2 Analytical data of metal complexes**

Compounds	Found %(Calc %)			
	C	H	N	M
$L_1 = C_{22}H_{24}N_4$	76.21(76.78)	6.85(6.98)	15.91(16.27)	—
$L_2 = C_{22}H_{22}N_4Br_2$	52.57(52.72)	4.36(4.22)	11.5(11.06)	—
$[Zn(L_1)(H_2O)_2]SO_4$	49.15(48.73)	5.26(5.16)	9.96(10.36)	11.83(12.04)
$[Zn(L_2)Cl_2]$	41.32(41.56)	3.46(3.44)	8.76(8.94)	10.24(10.10)

Table: -3 IR Spectra data of Schiff bases and their metal complexes.

Compounds	ν (C=N) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O/Cl) cm^{-1}
Schiff base (L_1) -	1630	—	—
Schiff base (L_2)	1642	—	—
$[Zn(L_1)(H_2O)_2]SO_4$	1625	454	510
$[Zn(L_2)Cl_2]$	1634	460	476

Table-4 :- Antimicrobial data of metal complexes

S.N	Compounds	Minimum inhibition concentration (mg/ml)				
		E.coli	S.aureus	B.subtilis	A.niger	F.Oxysporum
1.	Schiff base	4	6	-	7	9
2.	$[Zn(L_1)(H_2O)_2]SO_4$	8	12	9	10	11
3.	$[Zn(L_2)Cl_2]$	12	14	1 3	12	1 4

IR Spectra-

The IR spectrum of free ligand was compared with that of complexes in order to determine the coordination site are listed in Table 3. A very strong band around 1640 cm^{-1} is characteristics of the azomethine nitrogen (>C=N) present in the Schiff base ligand. This was shifted to 1634-1625 cm^{-1} in the complexes, which indicates the bonding of the metal to the azomethine nitrogen. A new band around 460 cm^{-1} in zinc complexes, which has been attributed to the ν (M-N) stretching vibrations.

Electronic Spectra of Metal Complexes:-

The electronic spectra of Zn(II) complexes show intra-ligand transition at 290 nm. Due to (t_2g)6 (eg)4 configuration of Zn(II) ion, all complexes are diamagnetic in nature.

Antimicrobial Activity: -

The ligand as well as complexes were screened for their in vitro antibacterial activity against Gram- positive bacteria (B. subtilis, S. aureus) and Gram- negative bacteria (E. coli) using disc diffusion method by taking DMSO as solvent. The in vitro antifungal activities of the ligand and its metal complexes have been tested against the fungi Aspergillus niger and Fusarium oxyporum by using disc diffusion method. The antimicrobial data of ligand and its metal complexes are presented in Table 5. A Comparative study of the growth inhibition zone values of Schiff base and its metal complexes indicate that metal complexes exhibit higher antibacterial and antifungal activity than the free Schiff base ligand. This is probably due to the greater lipophilic nature of the complexes. The activity of the ligand may be attributed to azomethine linkage in it. The increased activity of the metal complexes can be ascribed to the increase in lipophilic nature of complexes due to chelation.

CONCLUSION:

The coordination ability of Schiff bases has been reported by physical characteristics, micro-analytical data, FTIR and UV spectral data confirm the ligands is coordinating through azomethine nitrogen and two oxygen atoms of the water molecules or two chlorine atoms forming a six membered chelate. It is concluded that metal complexes show coordinated octahedral geometry. The ligand as well as its metal complexes are good activity against Gram-positive and Gram-negative bacteria and fungi.

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