

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MIXED LIGAND CHELATES WITH SCHIFF BASE AS PRIMARY LIGAND

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ABSTRACT

Mixed ligand chelates of Mn(II), Zn(II) and Cd(II) with Schiff base 2,5-dihydroxy-benzophenone thiosemicarbazone as primary ligand(L₁) and 2-pyridine ethanol as secondary ligand(L₂) have been synthesized and characterized by analytical data, molar conductance, magnetic measurements, electronic spectra, IR spectra and thermogravimetric analysis. Mn(II) chelate was found to have octahedral structure while Zn(II) and Cd(II) chelates possess distorted tetrahedral structure.

Keywords: *Mn(II), Zn(II) and Cd(II) Chelates, 2-Pyridine Ethanol, Schiff Base, Spectral Studies*

I. INTRODUCTION

Schiff bases are of the most widely used organic compounds and having remarkable applications in medical fields. They have been shown to exhibit a broad range of biological activities including antimicrobial, antiviral and antipyretic properties[1-3]. On coordination of metal ions to Schiff base improves their efficiency and hence their bioactivity[4-5]. Mixed ligand chelates play a very significant role in biological systems and have been a subject of great interest for researchers. A good deal of work has been reported on the preparation and structural investigation of Schiff bases and their chelates[6-8].

The present study will describe the synthesis of the Schiff base 2,5-dihydroxy-benzophenone thiosemicarbazone as primary ligand(L₁) which is used as primary ligand with 2-pyridine ethanol as secondary ligand(L₂) in mixed ligand chelates with Mn(II), Zn(II) and Cd(II) ions and characterized by elemental analyses, molar conductance, electronic, IR and thermogravimetric analysis.

II. EXPERIMENTAL

All chemicals used were of A.R grade. Elemental analyses were carried out on thermo quest analyzer. Metal contents were measured by EDTA titration. The conductivity measurements were made on Systronic conductometer model 303 using DMF. Magnetic moments were measured by Guoy method. IR spectra (KBr pellets) were recorded on a Perkin Elmer 577 grating IR spectrophotometer. Thermogravimetric analysis was performed by Perkin Elmer Thermal analyzer.

2.1 Synthesis of Schiff base

2,5-dihydroxybenzophenone was prepared by the literature method[9]. Its thiosemicarbazone was obtained by refluxing ethanolic solution with thiosemicarbazide in concentrated HCl for 3 hours on water bath. On cooling, a brown coloured compound separated out. It was filtered, washed with ethanol, dry ether and dried well under anhydrous conditions.

2.3 Preparation of Mn(II), Zn(II) and Cd(II) chelates

An ethanolic solution (25ml) of metal salts of Mn(II), Zn(II) and Cd(II) was added gradually to a stirred ethanolic solution of Schiff base(25ml) and secondary ligand 2-pyridine ethanol to get (1:1:1) molar ratio. The resulting solution was refluxed for about 4 hours on water bath. The chelate was precipitated, cooled and then filtered. The product obtained was washed with small amounts of ethanol and then dried in vacuum.

III. RESULTS AND DISCUSSION

The physical and CHN elemental analysis data of the synthesized chelates as shown in (Table 1) exhibit the formation of 1:1:1 [M:L1:L2] ratio. It was found that the theoretical values are in a good agreement with the found data. The resulted chelates are coloured solid and stable in air. They are insoluble in water and most of organic solvents but soluble in DMSO and DMF. Metal contents have been determined gravimetrically. Conductivity data of 10^{-3} M solution of Mn(II) chelate in DMSO suggested their non-electrolytic nature while that of Zn(II) and Cd(II) chelates correspond to 1:1 electrolytic nature. The electrolytic nature of Zn(II) and Cd(II) chelates is further confirmed by formation of white curdy precipitates on addition of alcoholic AgNO_3 to the solution of chelates in DMSO[9].

3.1 Magnetic Measurements

Mn(II) chelate shows magnetic moment value 5.95 B.M. lying in the range 5.70-6.00 B.M. indicating high spin octahedral geometry[10]. The magnetic moment value of Zn(II) and Cd(II) chelates is in the range of 0.18 to 0.24 B.M which shows their diamagnetic nature[11].

3.2 Electronic Spectra

Mn(II) chelate in DMF shows five bands in the range 18800-18950, 23600-24400, 25250-26300, 29100-29900 and 34800-35750 cm^{-1} corresponding to the spin-forbidden transitions from the ground state to ^4G , ^4P and ^4D excited state of the ion. These bands may be assigned to following transitions: $^6\text{A}_{1g}(\text{G}) \rightarrow ^4\text{T}_{1g}(\text{G})$; $^6\text{A}_{1g}(\text{G}) \rightarrow ^4\text{T}_{2g}(\text{G})$; $^6\text{A}_{1g}(\text{G}) \rightarrow ^4\text{E}_g(\text{G})$, $^4\text{A}_{1g}(\text{G})$; $^6\text{A}_{1g}(\text{G}) \rightarrow ^4\text{T}_{2g}(\text{D})$ and $^6\text{A}_{1g}(\text{G}) \rightarrow ^4\text{T}_{1g}(\text{P})$. These transitions suggest octahedral geometry for Mn(II) chelate. The calculated values of ligand field parameters also confirm the octahedral stereochemistry. The value of β is less than unity indicating covalent bond formed between metal atom and donor atom of the ligand. Zn(II) and Cd(II) chelates are found to be diamagnetic as expected for d^{10} system because d-d transitions are not possible hence electronic spectra did not give any fruitful information[12-13].

3.3 Infrared Spectra

The IR spectra of Mn(II) chelate exhibit bands in region $3400-3390\text{ cm}^{-1}$ and $850-860\text{ cm}^{-1}$ assignable to stretching and rocking modes of coordinated water molecule while a broad band around 3450 cm^{-1} in the spectra of Zn(II) and Cd(II) chelates indicates the presence of lattice held water molecule[14].

The spectra of chelates shows a band for azine at $1560-1580\text{ cm}^{-1}$ suggests coordination of metal ion through the azine nitrogen and thiol sulphur of enolic form of thiosemicarbazone. The N-N stretching band at $1040-1060\text{ cm}^{-1}$ in the spectra of Schiff base shows a positive shift and $\nu(\text{CH}=\text{N})$ at $1680-1650\text{ cm}^{-1}$ shifts to lower frequency region in the spectra of all the chelates. This confirms the bonding of metal ion with azomethine nitrogen of ligand. A band at 750 cm^{-1} corresponding to $\nu(\text{C}=\text{S})$ is observed in spectra of Schiff base. This band shifts to lower frequency region in the spectra of their chelates and thus assigned to $\nu(\text{C}-\text{S})$. A band observed at 3220 cm^{-1} assigned to νNH_2 in Schiff base, which remains unchanged, indicating the non-participation of the $-\text{NH}_2$ group. A broad band, due to phenolic $-\text{OH}$ at 3460 cm^{-1} in the spectra of ligand is observed almost at the same position in spectra of all the chelates but the intensity is found to be low in Mn(II) chelate, indicating that only a single $-\text{OH}$ group takes part in the reaction with Mn(II). The $\nu(\text{C}-\text{O})$ phenolic stretch shifts to higher energy by 10 cm^{-1} in Mn(II) chelate indicating coordination of phenolic $-\text{O}$ with Mn(II) ion while in Zn(II) and Cd(II) chelates, the phenolic $-\text{OH}$ frequency remains unchanged indicating the non- participation of phenolic $-\text{OH}$ group of Schiff base[14].

A strong band in the spectrum of 2-pyridine ethanol ligand at $1620-1640\text{ cm}^{-1}$ assigned to $\nu(\text{C}=\text{N})$ shifts to lower energy side $10-20\text{ cm}^{-1}$ in the spectra of chelates. This indicates the coordination of nitrogen to the metal ion. An additional band at $\sim 260\text{ cm}^{-1}$ in the spectra of all the chelates also confirms the coordination of pyridine - nitrogen with the metal ion. A medium band existing in the spectrum of 2-pyridine ethanol at 3250 cm^{-1} shows a positive shift in all the chelates. This suggests the coordination of metal ion through oxygen of 'OH' group.

Some new non-ligand bands appeared in the far IR region around $500-300\text{ cm}^{-1}$ has been noticed in spectra of all the chelates. These bands are assigned to $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{S})$, respectively. Zn(II) and Cd(II) chelates exhibit an additional band around 240 cm^{-1} which may be assigned to $\nu(\text{M}-\text{Cl})$ vibrations[15].

3.4 Thermogravimetric Analysis

The weight loss observed by TG analysis of Mn(II) chelate at temperature 175°C corresponds to the elimination of one molecule of water and supports further the presence of one coordinated water molecule while Zn(II) and Cd(II) chelates show the weight loss equivalent to one water molecule at about 90°C which indicates the presence of only one lattice held water molecule[17].

3.5 Evaluation of Antimicrobial Activity

Mn(II), Zn(II) and Cd(II) mixed ligand chelates have been screened for their inhibitory effects against four organism viz S.aureus, B.megaterium, B.cereus (gram positive) and E.coli (gram negative) by cup plate method. The zones of inhibition have been measured and the activity results regarding the ligands and their chelates have been recorded[18,19].

IV. CONCLUSION

Spectral studies reveals that primary ligand Schiff base acts as tridentate in Mn(II) chelate and bidentate in Zn(II) and Cd(II) chelates while secondary ligand 2-pyridine ethanol serve as bidentate ligand in all the chelates under study. TG data confirms coordination of one water molecule in Mn(II) chelate and presence of one lattice held water molecule in Zn(II) and Cd(II) chelates. The results of the evaluation of antimicrobial activity showed that all the synthesized chelates exhibit considerable activities towards all the four pathogenic bacteria. The activity of chelates was found to be greater than those of the metal salts and ligands. The increased activity of chelates might be due to the combined activity effect of both the ligands present. In addition, it has been noticed that thiosemicarbazone ligand showed less activity towards E.coli. On the basis of elemental analysis, magnetic moment data, conductivity measurements, electronic spectra, IR spectra and thermogravimetric analysis, the geometry of Mn(II) chelate is suggested as octahedral while that of Zn(II) and Cd(II) chelates as distorted tetrahedral as shown in Fig.1 and Fig.2.

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Table – 1 Analytical data of Mn(II), Zn(II) and Cd(II) mixed ligand chelates

S. No	Chelates	% chemical analysis; found (calculated)						μ_{eff} (B.M.)	Ω_m in DMSO ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Colou r M.P. ($^{\circ}\text{C}$)	Mol. Wt. Found (Calcd.)
		C	H	N	S	Cl	Metal				
1	[Mn(L ₁)(L ₂)H ₂ O]	51.40 (52.39)	4.32 (4.15)	11.12 (11.64)	7.00 (6.65)	--	11.10 (11.42)	5.95	16.72	Brown 195	460.80 (480.94)
2	[Zn(L ₁)(L ₂)Cl.H ₂ O]	46.65 (47.82)	4.10 (3.79)	10.28 (10.62)	6.25 (6.07)	6.15 (6.73)	12.63 (12.41)	Diamagn etic	82.85	Cream 135	505.60 (526.89)
3	[Cd(L ₁)(L ₂)Cl.H ₂ O]	42.85 (43.91)	3.65 (3.48)	10.15 (9.75)	6.00 (5.57)	6.25 (6.18)	20.05 (19.58)	Diamagn etic	84.55	Light yellow 147	535.6 (573.9)

Table – 2 Main IR Bands (cm^{-1}) observed in the Spectra of Mn(II), Zn(II) and Cd(II) mixed ligand chelates

S. No	Chelates	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}-\text{N}=\text{C})$	$\nu(\text{C}-\text{S})$	$\nu(\text{N}-\text{N})$	$\nu(\text{OH})$ L ₂	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
1	[Mn(L ₁)(L ₂)H ₂ O]	1630	1570	740	1040	3280	470	500	320	---
2	[Zn(L ₁)(L ₂)Cl.H ₂ O]	1650	1580	750	1060	3270	470	510	310	250
3	[Cd(L ₁)(L ₂)Cl.H ₂ O]	1640	1560	740	1050	3290	460	500	300	260

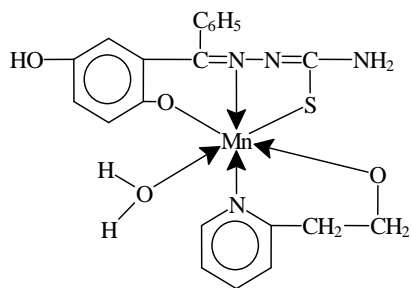


Fig.1

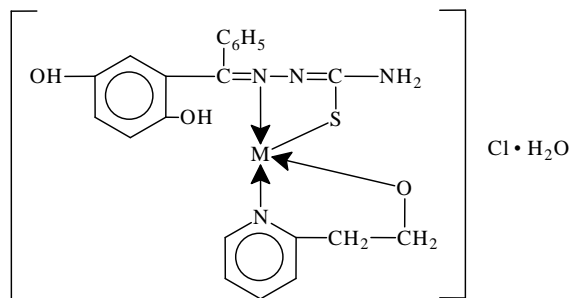


Fig. 2 (where M = Zn(II)/Cd(II))