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Synthesis, Spectral and Antimicrobial Activity of Zn (II), Cd (II) and Hg (II) Complexes of Some Quinoxaline Schiff Bases

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Abstract: The complexes Zn(II), Cd(II) and Hg(II) of Quinoxaline based Schiff Bases derived from the condensation reaction of 3-Chloro-2-hydrazinoquinoxaline with 2-Hydroxybenzaldehyde and 2-Hydroxy-3-methoxybenzaldehyde have been prepared and characterized. These two ligands function as uni-negative bidentate co-ordinating ligand with Zn(ii), Cd(II) and Hg(II) ions through phenolic oxygen and free azomethine nitrogen ($\nu\text{C}=\text{N}$). The geometry and the bonding characteristics associated with the complexes have been deduced from the relevant spectral data. Further, the ligands and their Zn(ii), Cd(II) and Hg(II) complexes have been screened for their antibacterial and antifungal activity and the results are presented.

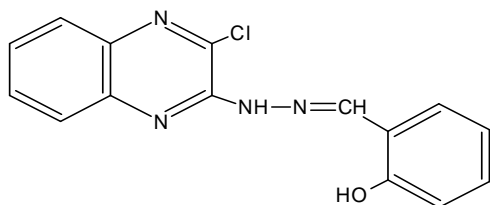
Key words: Metal complexes, Quinoxaline based Schiff bases, Synthesis, Spectral studies, antimicrobial activity

Introduction:

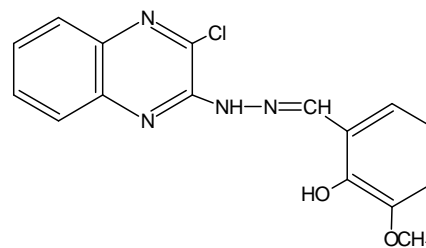
Quinoxalines are a class of fused six-membered nitrogen heterocyclics containing two nitrogens in mutually para disposition. These compounds have a wide range of applications in pharmacology, bacteriology and mycology^[1-7].

Quinoxaline and its derivatives have received attention as complexing agents owing to the presence of two potentially metal binding nitrogen centers at 1,4 positions. Further, significant chelating abilities could be developed in these systems by introducing suitable substituents in the heterocyclic ring or benzene ring.

Metal complexes of various Quinoxaline derivatives have been synthesized and characterized over the years. Quinoxalines attract an immense interest because of their diverse pharmacological applications. Owing to the importance associated with this class of compounds. We present herein the synthesis and characterization of Zn(II), Cd(II) and Hg(II) complexes of Quinoxaline-based Schiff bases namely 2-Hydroxybenzaldehyde-1-(3-chloro-2-quinoxaliny)hydrazone (HBCQOH) and 2-Hydroxy-3-methoxybenzaldehyde-1-(3-chloro-2-quinoxaliny)hydrazone (HMBCQH)



HBCQOH



HMBCQH

Experimental:

All the chemicals used were of A.R or B.D.H grade. The ligands HBCQOH and HMBCQH were prepared by stirred an equimolar mixture of 3-Chloro-2-hydrazinoquinoxaline⁸ with 2-Hydroxy benzaldehyde and 2-hydroxy-3-methoxy benzaldehyde in DMF at room temperature for about 2 hours. When the solid separation completed, it was filtered, washed with water and recrystallized from CHCl_3 -hexane. The colour, yield %, m.p($^{\circ}\text{C}$) and elemental analysis(%) of HBCQOH and HMBCQH are respectively, yellow 68; 175-176 $^{\circ}\text{C}$; [Found(%) C,59.72; H,3.54; N,18.39; $\text{C}_{15}\text{H}_{11}\text{N}_4\text{OCl}$ requires C,60.31; H,3.71; N,18.75] and bulk yellow, 72; 214-216 $^{\circ}\text{C}$; [Found(%) C,58.09; H,3.83; N,16.85; $\text{C}_{16}\text{H}_{13}\text{N}_4\text{O}_2\text{Cl}$ requires C,58.46; H,3.99; N,17.04];

The Zn(II) and Cd(II) complexes with the two ligands were prepared using respective metal acetates and Hg(II) complexes using respective metal chlorides. In the preparation of all the metal complexes, the metal and the ligand were combined in 1:2 mole ratio (the metal being in slight excess of what the ratio required) using required quantities of methanol or aqueous methanol for the metal salts and methanol for the ligands so as to effect their solubility. The contents were refluxed on a water bath for 2-3 hours and the solid that separated was filtered, washed with water, hot methanol and ether and dried in air. The elemental analyses were carried out by Carlo Erba 1108 elemental analyzer at RSIC, CDRI, Lucknow. Conductance measurements on the complexes were made in DMF at 10^{-3} M concentration on a Digisun digital conductivity meter,

DI 909 model with a cell calibrated with 0.1M KCl solution was employed to measure conductance of the metal complexes in DMF at 10^{-3} M concentration. The magnetic susceptibilities of the complexes were recorded on a Faraday balance (CAHN-7550-03) at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the standard.

Diamagnetic corrections were applied using Pascals's constants⁹. The infrared spectra of the ligands and the metal complexes were recorded in KBR pellets in the range $4000\text{--}400\text{cm}^{-1}$ on Perkin Elmer-BX spectrophotometer at central Instrumentation center, Kakatiya University. The electronic spectra of the metal complexes in DMF were recorded on ELICO SL-159 UV-Vis spectrophotometer. The $^1\text{H-NMR}$ spectra of the ligands were recorded in DMSO-d_6 solution employing Bruker avance 300 MHz and Variangemini 200 MHz.

The Chemical shifts are given in ppm downfield from tetramethylsilane.

Results and discussion:

All the metal complexes are coloured, stable at RT and are non hygroscopic. They are insoluble in water and soluble in DMF and DMSO. All the metal complexes which are non –electrolytic in DMF give satisfactory C,H,N and M analyses corresponding to 1:2 metal-organic ligand stoichiometry. The magnetic studies reveal that Zn(II), Cd(II) and Hg(II) complexes have all been found to have no magnetic moment and so are diamagnetic in nature.

The molar conductance values observed for the present Zn(II), Cd(II) and Hg(II) complexes of HBCQOH and HMBCQH in dimethylformaamide at 10^{-3} M concentration are given in Table-1.

Table-1: Molar conductance ($\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$) data for the present metal complexes:

S.No.	MetSal complex	Molar conductance
(1)	(2)	(3)
1	$[\text{Zn}(\text{HBCQOH-H})_2]$	13
2	$[\text{Cd}(\text{HBCQOH-H})_2]$	10
3	$[\text{Hg}(\text{HBCQOH-H})_2]$	14
4	$[\text{Zn}(\text{HMBCQH-H})_2]$	12
5	$[\text{Cd}(\text{HMBCQH-H})_2]$	10
6	$[\text{Hg}(\text{HMBCQH-H})_2]$	10

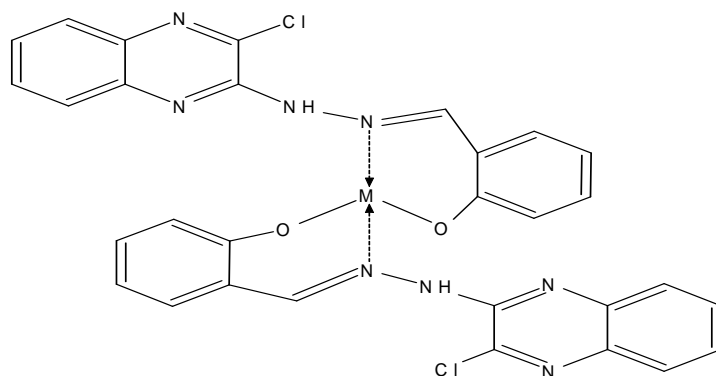
In examination of the data in table indicates at the Zn(II), Cd(II) and Hg(II) complexes are non electrolytes. In the HBCQOH and HMBCQH show in their spectra a medium intensity band in the region $3200\text{--}3330\text{cm}^{-1}$ that has been assigned to $\nu\text{O-H}$. This band disappears in the spectra of their complexes indicating that deprotonation of the group has taken place. A small or medium intensity band around 1230cm^{-1} in the ligands assignable to $\nu\text{C-O}$ is seen to have undergone a positive shift by $30\text{--}50\text{cm}^{-1}$ in the complexes suggesting coordination through phenolic oxygen¹⁰. The positive shift observed may be attributed to the drift of electron density from oxygen to the metal ion resulting in greater ionic character of the C-O bond and a consequent increase in its vibration frequency^[11]. The ligands record a somewhat broad, medium intensity band around 3430cm^{-1} attributable to free $\nu\text{N-H}$ ¹². This band remains either unshifted or higher shifted in the complexes indicating nonparticipation of nitrogen of this group in coordination. Further, the ligands reveal bands around 1620cm^{-1} due to free $\nu\text{C=N}$ and around 1580cm^{-1} due to ring $\nu\text{C=N}$. While the band due to free $\nu\text{C=N}$ has got

lower shifted by $10\text{--}20\text{cm}^{-1}$ in all the complexes, the band due to ring $\nu\text{C=N}$ is unshifted in Zn(II), Cd(II) and Hg(II) complexes. This suggests that the ligands act as mononegative, bidentate ones bonding through phenolic oxygen and nitrogen of free C=N group^[13-15].

A comparison of the $^1\text{H-NMR}$ spectra of the ligands and Zn(II) complexes clearly indicates deprotonation of phenolic OH during complexation.

The present Zn(II), Cd(II) and Hg(II) complexes show no d-d bands in their electronic spectra and on the basis of analytical, conductance and infrared spectral data, the complexes have been assigned tetrahedral geometry – the most preferred geometry for a tetra-coordinated d^{10} system.

The biological activity of these compounds, endowed with potential bonding sites, may be attributed to their ability to chelate metal ions present in the biosystem; sometimes, the metal ion association exerts synergistic effect on the activity of the free ligand in which case, a metal complex formed of a ligand is found more active



M= Zn, Cd or Hg

Structure of Zn(II), Cd(II) and Hg(II) complexes of HBCQOH

than the free ligand. Considering these observations, the biological activity studies have been undertaken in which the representative ligand HBCQOH and its VO(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and Hg(II) complexes have been screened for antimicrobial activity against the bacteria: *Staphylococcus aureus* (gram+ve) and *Escherichia coli*

(gram -ve) and fungus: *Fusarium oxysporum*. The compounds were assayed for their antibacterial and antifungal activities by seeded plate technique [28].

The results of the antibacterial and antifungal screening of the compounds are presented in tables 2 and 3 respectively.

Table-1: Antibacterial activity of the compounds

Solvent:Acetone

Concentration: 0.1 mg/ml

S.No.	Compound	Zone of inhibition (mm)	
		Staphylococcus aureus (Gram +ve)	Escherichia coli (Gram -ve)
1.	HBCQOH	---	---
2.	Zn-HBCQOH	2.5	4.0
3.	Cd-HBCQOH	3.5	---
4.	Hg-HBCQOH	11.0	6.5
5.	Streptomycin sulphate (standard)	15.0	14.5

Table-3; Antifungal activity of the compounds

Solvent: Acetone

Concentration: 0.1 mg/ml

S.No.	Compounds	Percentage of inhibition <i>Fusarium oxysporum</i>
1.	Medium (Control)	****
2.	HBCQOH	***
3.	Zn-HBCQOH	---
4.	Cd-HBCQOH	---
5.	Hg-HBCQOH	---

**** No inhibition (Full growth) *** 25% inhibition

** 50% inhibition * 75% inhibition

--- 100% inhibition

The results on the antibacterial activity of the compounds screened indicate that the ligand HBCQOH of Zn and Hg complexes are active on the microorganisms, to a different level, of course, against both the bacteria, the others are so either with gram +ve or with gram -ve. The Hg complex, of all, has been found most active. The antifungal results indicate that the metal complexes do, in general, well in that many of

them are either more active than or as active as their ligand. The metal complexes of Zn, Cd and Hg are more active.

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