

Synthesis And Characterization of Mn (II), Co (II), Ni (II), Cu (II) And Zn (II) Complexes Derived from 3-((3-Hydroxyphenylimino) Methyl) Quinoxalin-2-Ol

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Abstract: Mn(II),Co(II),Ni(II), Cu(II) and Zn(II) Complexes of 3-((3-hydroxyphenylimino) methyl)quinoxalin-2-ol (HIMQ) has been prepared and characterized by elemental analysis, Conductivity measurement, Magnetic property, Infra Red spectrum, electronic spectrum, Thermal analysis on the basis of spectral data (HIMQ) deprotonates to give monobasic ONO donor and binds to Cu(II) and Zn(II) in tetradentate fashion and to Mn(II), Ni(II), Co(II) in hexadentate fashion. The molar conductivity data revealed that all complexes are in non ionic nature.

Keywords: Schiff bases, 3-Hydroxyquinoxaline-2-carboxaldehyde, 3-amino phenol, 3-((3-hydroxyphenylimino) methyl) quinoxalin-2-ol, Metal Complexes, Spectral Studies.

Introduction

Schiff bases are widely used for synthetic purposes both by organic and inorganic chemists. In addition, Schiff bases show numerous biological activities including antibacterial, antifungal, and antitumor and antiherbicidal activities. Such bases are also used as ligands for complex formation with some transition and non-transition metal ions¹.

Quinoxaline² also known as 1, 4-benzodizine, benzoparidiazine, phenpiazine or benzopyrazine is a heterocyclic compound in which a benzene ring is fused with pyrazine ring. Quinoxaline and its derivatives constitute an important class of nitrogen containing heterocycles. The presence of hetero atoms in their ring and extended π -conjugation causes decrease in columbic repulsion. Derivatives of Quinoxaline are widely used as bridging ligand in both homobimetallic and heterobimetallic complexes. They have wide variety of biological applications³⁻¹⁰ including in optoelectronic devices¹¹⁻¹² self extinguishing and flame resistance polymer, flourophores¹³⁻¹⁶ photo sensitizers, corrosion inhibitor and electron transport material.

The present work deals specially the coordination properties of 3-((3-hydroxyphenylimino) methyl) quinoxalin-2-ol¹⁷ concerning its interaction with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II). In this work spectral characterization serves as an important tool for the interpretation of structures. All the complexes were characterized on basis of elemental analysis, Conductivity measurement, Magnetic property, Infra Red spectrum, electronic spectrum, Thermal analysis.

Materials and Methods

All the chemicals used were analytical reagent grade and purchased from Spectrochem, Loba or sdfine chemicals. The solvents used were of high purity and distilled in laboratory before use. Thin layer chromato

graphy was carried out on silica gel 60/UV254. Melting points of products were recorded in open capillaries on digital melting point apparatus (optics technology) and were uncorrected.

IR spectra were recorded on Perkin-Elmer FTIR Spectrophotometer in range 4000-500 cm^{-1} using ATR Instrument. Samples were kept directly without KBr pallets. ^1H NMR spectra were obtained on a Perkin-Elmer 300 MHz spectrophotometer using TMS as internal standard in DMSO- d_6 as the solvent.

Elemental analysis was performed on elementar vario EL-III at SAIF Kochi. The percentage of Metal was determined by EDTA complexometric titration. TGA-DTA of complexes studied by Perkin-Elmer Diamond at STIC Cochin University Kochi. Conductance of complexes were determined in DMSO on conductivity meter Equiptronics model No.EQ665. Magnetic measurements were done on solid complexes using Guy Balance.

Experimental

Synthesis of Schiff base:

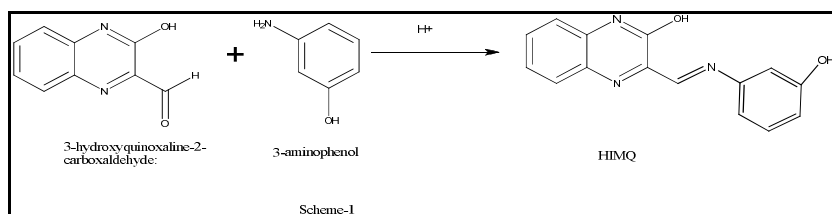
The synthesis of Schiff bases involved into two main stages namely synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde and the subsequent condensation of these aldehydes with 3-amino phenol. 3-Hydroxyquinoxaline-2-carboxaldehyde was synthesized by reported method¹⁸

Preparation of 3-((3-hydroxyphenylimino) methyl) quinoxalin-2-ol :(HIMQ)

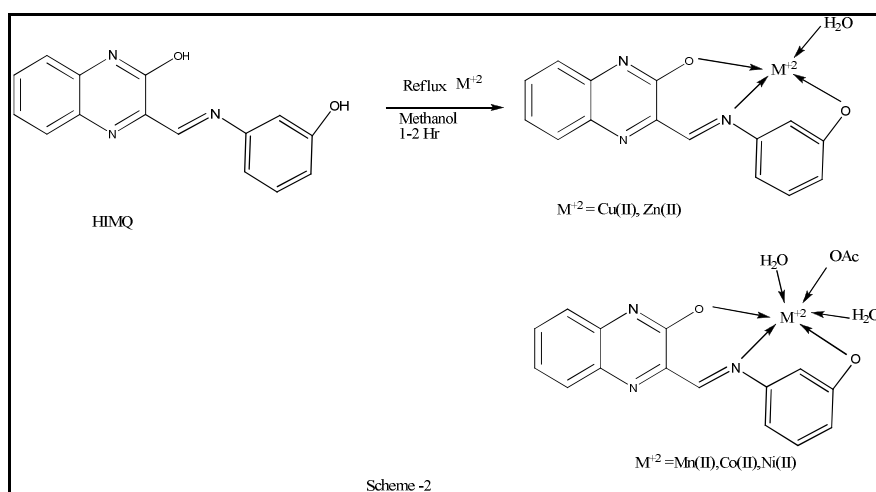
The 3-hydroxyquinoxaline-2-carboxaldehyde solution was made 0.025 molar with respect to HCl. Ethanolic Solution of 3-aminophenol (1.09 gm 0.001 mol) was added to this dropwise with constant stirring. The amino pyridine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with ethanol and dried in *vacuo* over anhydrous calcium chloride (Yield: 50-65%, M.p: 250 $^{\circ}$ C).

Anal. Cald. For $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}_2$ (264.78) C (72.72%) H (4.58%) N (10.60%) O (12.11%) IR: 3362, 3170, 2918, 1658, 1613, 1495, 1191, 753 cm^{-1} NMR δ ppm: (300 MHz, DMSO- d_6 , 297 K) δ =6.04 (Ph-OH, s, 1H), 6.21 to 7.98(ArH, m, 8H), 8.97(HC=N, s, 1H), 12.58

(OH, s, 1H).



Preparation of complex of HIMQ:



The Schiff base HIMQ (0.01 mol, 0.250 gm) was dissolved in 50ml methanol to this solution metal salt (0.01mol; manganese acetate tetra hydrate 0.245gm, Cobalt acetate hex hydrate 0.249gm, Nickel acetate 0.249gm, Cupric acetate 0.219gm, Zinc acetate 0.198gm) in 20ml water was added. The solution was refluxed for an hour and then kept at room temperature after reducing volume by evaporation precipitate formed was filtered, washed with ethanol and kept in desiccators.

Results and Discussion

The complexes were stable in air and non hygroscopic. They are soluble in DMSO. The analytical data in (Table 1) reveals that all complexes formed in metal: ligand ratio of 1:1. Further the molecular formula of the complexes given in the table agrees well with the analytical data. Very low conductance values of the complexes in DMSO indicate the non-electrolytic nature of the complexes¹⁸. The magnetic moment values (30⁰C) of the complexes are given in (Table 1). μ_{eff} value of Mn(II) complex was found to be 5.17 B.M. as expected to high spin d⁵ system. The Co (II) complex has magnetic moment of 4.80 B.M. as expected for high spin Co (II) higher magnetic moment is due to orbital contribution¹⁹. The Ni (II) complex exhibit s a magnetic moment value of 3.80 B.M. which is in the normal range observed for tetrahedral Ni (II) complexes. The magnetic moment of the copper (II) complex is 2.11 B.M. which suggest absence of Cu-Cu interactions. The higher value suggests tetrahedral structure.

Table- 1: Analytical and physical data of HIMQ and their metal complexes.

Code	Ligand/ Complex	Colour	% Yield	M.P. in (⁰ C)	Elemental Analysis Found (calc.) %				μ_{eff} B.M.	Molar *cond uct.
					C	H	N	M		
L1	HIMQ	Dark Yellow	80	250	72.72 (71.12)	4.58 (4.68)	15.84 (14.54)			
1	[Mn(HIMQ)H ₂ O]H ₂ O	Brown	47	>300	56.37 (55.32)	3.62 (3.56)	11.60 (10.98)	15.18 (15.70)	5.17	8.5
2	[Co(HIMQ)(OAc) (H ₂ O) ₂]H ₂ O	Brick Red	72	>300	55.75 (55.02)	3.56 (3.10)	11.47 (11.01)	16.09 (16.26)	4.8	6.02
3	[Ni(HIMQ)(H ₂ O)]H ₂ O	Brick Red	64	>300	55.06 (54.67)	3.53 (3.80)	11.33 (11.98)	17.14 (17.43)	3.8	8.3
4	[Cu(HIMQ)(H ₂ O)]	Black	82	>300	54.91 (54.95)	3.79 (3.71)	11.30 (10.98)	17.09 (17.18)	2.11	7.18
5	[Zn(HIMQ)(H ₂ O)]	Orange	74	>300	54.63 (54.35)	3.78 (3.76)	11.24 (11.92)	17.50 (17.66)	Dia.	7.4

*Molar conductivity (in Mho cm² mol⁻¹) 10⁻³ Molar solution in DMSO

IR spectra:

The IR spectra of Schiff bases under study are recorded in solid state selected bands of diagnostic importance were collected in (Table2). A new broad band at 3350 cm⁻¹ is seen for all complexes which may be due to presence of hydrated or coordinated water molecule [20]. The azomethine C=N stretching was observed at lower frequency than that for ligand. This negative shift in C=N indicates coordination of nitrogen. Appearance of new bands in the spectra of all complexes in the regions 500-450 and 420-400 cm⁻¹ has been attributed to ν (M-O) and ν (M-N) stretching respectively.

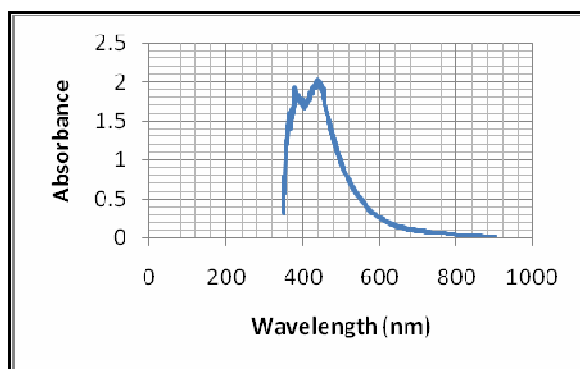
Electronic Spectra:

Electronic spectra of ligand and complexes were taken in DMSO (5*10⁻⁴ molar) and shown in (Table 2) The ligand shows absorptions at 250nm and 400nm due to π - π^* transition in benzene, π - π^* transition in quinoxaline and π - π^* transition in imino group and n- π^* transition in ligand . In complexes, the intense bands above 400nm were observed due to charge transfer and interligand transitions. In the electronic spectrum of Co (II) complex the d-d transition are almost masked by high intensity charge transfer bands shoulder is observed around 427nm which may be assigned to the ⁴T_{1g}(F) to ⁴T_{1g}(P) transitions it is reported for octahedral Co(II)

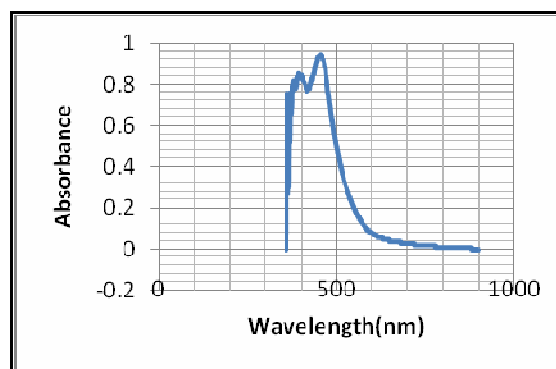
complexes²¹. The solution spectrum of Ni (II) complex shows charge transfer bands at 26109 cm⁻¹. The d-d bands are observed at 22831cm⁻¹ which is due to ³T₁-³T₂ and ³T₁-³T₁(P) transitions.

Table 2: Infrared, electronic spectra of PIMQ and their complexes.

Code	I.R. Values (cm ⁻¹)								Electronic Spectra (nm)
	ν (OH)	ν (N=CH)	ν (C=N)	ν (C=N)	δ (N=CH)	γ (C=N)	ν (M-O)	ν (M-N)	
	Free			ring					
L1	3362	2918	1668	1613	1235	1191	-----	-----	282,380
1	3375	2971	1649	1550	1259	1068	470	418	416,463
2	3207	2918	1604	1523	1312	1017	490	419	427,479
3	3107	2910	1664	1605	1200	1016	489	414	383,438
4	3253	2910	1665	1538	1220	1016	492	415	384,430
5	3176	2850	1662	1606	1197	1015	487	417	379,442



[Co (HIMQ)(OAc)(H₂O)₂]H₂O



[Zn (HIMQ)(H₂O)]

Thermal analysis

TGA data in the temperature range 40-300⁰C is given in (Table 3). The loss of lattice water molecule occurs in all complexes below 100⁰C. Loss of coordinated water in these complexes occurs in range 150-250⁰C. In the case of Ni (II) complex, the weight loss corresponding to one lattice water and two coordinated water occurs continuously. Above 250⁰C organic part of complexes begins to decompose Mn(II),Cu(II), Zn(II) complexes show four step decomposition while Co(II) show three step and Ni(II) complex decompose in five steps.

Table 3: Thermo gravimetric analysis data below 300⁰C

Complex	Temperature	Weight Loss	Fragment	Nature of
	Range, ⁰ C	In mg	Loss	Fragment
[Mn(HIMQ)OAc(H ₂ O) ₂]H ₂ O	55.12	0.04	1H ₂ O	Lattice water
	168.72	0.07	2H ₂ O	Coordinated Water
[Co(HIMQ)(OAc)(H ₂ O) ₂]H ₂ O	55	0.04	1H ₂ O	Lattice water
	168.72	0.078	2 H ₂ O	Coordinated
[Ni(HIMQ)OAc(H ₂ O) ₂]H ₂ O	62.95	0.04	1H ₂ O	Lattice water
	187.74	0.07	2H ₂ O	Coordinated Water
[Cu(HIMQ)(H ₂ O)]	205	0.18	1H ₂ O	Coordinated Water
[Zn(HIMQ)(H ₂ O)]	235	0.16	1H ₂ O	Coordinated Water

Conclusion

Synthesis and characterization of complexes of (HIMQ) with Mn (II), Co(II), Ni(II), Cu(II), Zn(II) is given and various physical, chemical and spectral parameters is studied. High decomposition points of complexes suggest good thermal stability at normal conditions. Molar conductivities of the complexes in DMSO suggest that complexes are nonelectrolytic in nature. The analysis suggest tetrahedral structure for Cu(II) and Zn(II) complexes while Mn(II),Co(II) and Ni(II) complexes has octahedral structure.

Acknowledgments

The authors are thankful to Director National Chemical Laboratory Pune for providing facility of ¹H NMR and to Principal Milliya college Beed fo providing facility of UV Spectroscopy..Authors also thankful to SAIF Cochin for providing Elemental analysis and TGA-DTA data. Authors also wish to extend their gratitude to the Principal, Balbhim Arts Science and Commerce College Beed for providing necessary laboratory facilities.

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