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Synthesis and characterization of Mn (II), Co(II), Ni(II), Cu(II) and Zn(II) complexes derived from 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol

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ABSTRACT

Mn (II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes of 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol (PIMQ) 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 (PIMQ) deprotonates to give monobasic ONN donor and binds to Mn(II), Ni(II), Cu(II) and Zn(II) in tetradentate fashion and to 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, 2-amino pyridine, 3-[(pyridine-2-ylimino) 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 ions [1].

Quinoxaline [2] also known as 1, 4-benzodizine, benzopardiazine, 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 applications [3-10] including in optoelectronic devices [11-12] self extinguishing and flame resistance polymer, flourophores [13-16] photo sensitizers, corrosion inhibitor and electron transport material.

The present work deals specially the coordination properties of 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol [17] 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 chromatography 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 elemental 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.

1.1 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 this aldehydes with 2-amino pyridine.

1.1.1 Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde:

The synthesis of aldehyde involves preparation of 3-hydroxy-2-methylquinoxaline, 3-hydroxy-2-dibromomethyl quinoxaline and subsequent conversion of the latter into the aldehyde.

1.1.1.1 Preparation of 3-methylquinoxaline-2-ol: Pyruvic acid (8.8 gm, 0.1 mol) was added with constant stirring to the solution of orthophenylenediamine (10.8 g, 0.1 mol) in 250 ml of distilled water. After completion of the reaction as indicated by TLC; the precipitated pale yellow colored solid was filtered, washed with water and dried. The crude product was recrystallised from 50% absolute ethanol. Yield: (90%, 14.4 g): Color: pale yellow; no sharp melting point. The compound decomposes within the range 212-225 $^{\circ}\text{C}$ accompanied by change in color pale yellow to light brown.

1.1.1.2 Preparation of 3(bromomethyl) quinoxalin-2-ol: To the solution of 3-methyl quinoxaline 2-ol (13.6 gm 0.1mol) in glacial acetic acid (200 ml), 10% (v/v) bromine in glacial acetic acid (110 ml) was added dropwise with constant stirring. The mixture was then exposed to sun light for 1 hrs with occasional stirring and then poured into water and precipitated dibromo compound was filtered off, washed with water and dried. The crude product was purified by recrystallisation 50% absolute ethanol. Yield: (92%, 29.3 g): Color: pale yellow; no sharp melting point but decomposes within the range 210-222 with a color changing from pale yellow to light brown.

1.1.1.3 Preparation of 3-hydroxyquinoxaline-2-carboxaldehyde:

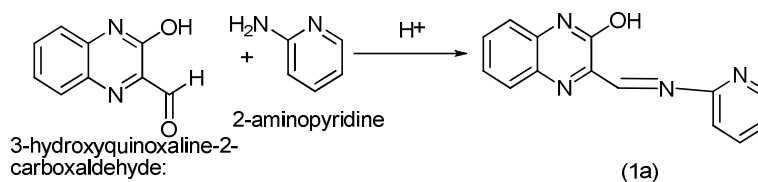
The dibromo compound (5 g, 0.01 mol) was thoroughly mixed with precipitated calcium carbonate (20 g) using mortar and pestle. The ensuing mixture was refluxed with distilled water (500 ml) for 3 hrs Occasional shaking and the aldehyde remaining in the solution was collected by filtration. The yellow colored aqueous solution thus obtained was stable and could be used for the preparation of Schiff base. The aldehyde was obtained as a fine yellow powder by concentrating the aqueous solution on rotary evaporator, extracting the aldehyde with ether, drying the ether extract with anhydrous sodium sulphate and removal of ether with rotary evaporator.

Color: yellow; no sharp melting point. The aldehyde decomposes within the range 108-130 $^{\circ}\text{C}$ and the color is changed from yellow to light brown. The yellow solid is not stable and changes its color to light brown in air indicating oxidation/decomposition of the aldehyde. However the aqueous solution of the aldehyde is stable. Therefore, it would be better to use the aldehyde solution for the synthesis of Schiff base.

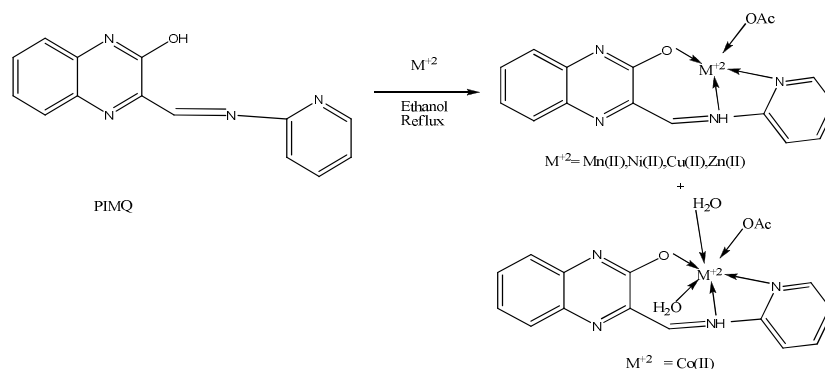
1.1.2 Preparation of 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol :(1a) (PIMQ)

The aldehyde solution was made 0.025 molar with respect to HCl. Aq. Solution of 2-aminopyridine (0.94 gm 0.001 mol) was added to this drop by drop while solution was stirred. 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: 50-60%, M.P.: 254 $^{\circ}\text{C}$).

Anal. Cald. For $C_{14}H_{10}N_4O$ (250.25), C(67.19%), H(4.03%), N(22.39%), O(6.39%) IR:3537, 3351, 3097, 2836, 1673, 1599, 1487, 1435, 1069, 770 cm^{-1} . NMR δ p.p.m.: (300 MHz, DMSO- d_6 , 297K) δ =5.86 to 8.00(ArH, m, 8H), 10.87(HC=N, s, 1H), 12.53(OH, s, 1H).

Scheme 1a:**1.1.3 Preparation of complex of PIMQ:**

The Schiff base PIMQ (0.01 mol, 0.250 gm) was dissolved in 50ml ethanol 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.

Scheme 1b:**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 complexes [18]. The magnetic moment values (30⁰C) of the complexes are given in (Table 1). μ_{eff} value of Mn(II) complex was found to be 5.12 B.M. as expected to high spin d^5 system. The Co (II) complex has magnetic moment of 4.92 B.M. as expected for high spin Co (II) higher magnetic moment is due to orbital contribution [19]. The Ni (II) complex exhibit s a magnetic moment value of 3.82 B.M. which is in the normal range observed for tetrahedral Ni (II) complexes. The magnetic moment of the copper (II) complex is 2.12 B.M. which suggest absence of Cu-Cu interactions. The higher value suggests tetrahedral structure.

2.1 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.

Table 1: Analytical and physical data of PIMQ and their metal complexes

Code	Ligand/ Complex	Colour	% Yield	M.P. in ($^{\circ}$ C)	Elemental Analysis Found (calc.) %				μ eff B.M.	Molar *conduct.
					C	H	N	M		
L1	PIMQ	Yellow	70	254	67.19 (68.02)	4.03 (4.08)	22.39 (22.54)	-	-	-
1	[Mn(PIMQ)H ₂ O]H ₂ O	Yellow	45	>300	55.18 (54.12)	3.76 (3.80)	16.09 (16.67)	15.78 (15.70)	5.12	8.31
2	[Co(PIMQ)(OAc)(H ₂ O) ₂]H ₂ O	Brown	70	>300	24.56 (25.02)	3.72 (3.10)	15.91 (16.01)	13.15 (13.26)	4.92	6.08
3	[Ni(PIMQ)(H ₂ O)]H ₂ O	Brown	63	>300	54.60 (54.67)	3.72 (3.80)	15.92 (15.98)	15.12 (15.43)	3.82	8.12
4	[Cu(PIMQ)(H ₂ O)]	Black	82	>300	53.85 (53.95)	3.67 (3.71)	15.70 (15.80)	17.77 (17.18)	2.12	7.17
5	[Ni(PIMQ)(H ₂ O)]	Dark Brown	72	>300	53.57 (53.80)	3.65 (3.70)	15.62 (15.92)	18.20 (18.67)	Dia.	7.42

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

2.2 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 230nm and 500nm due to π - π^* transition in benzene, π - π^* transition in quinoxaline and π - π^* transition in imino group. In complexes, the intense bands above 300nm 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 230nm which may be assigned to the ${}^4T_{1g}(F)$ to ${}^4T_{1g}(P)$ transitions it is reported for octahedral Co(II) complexes[21].

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

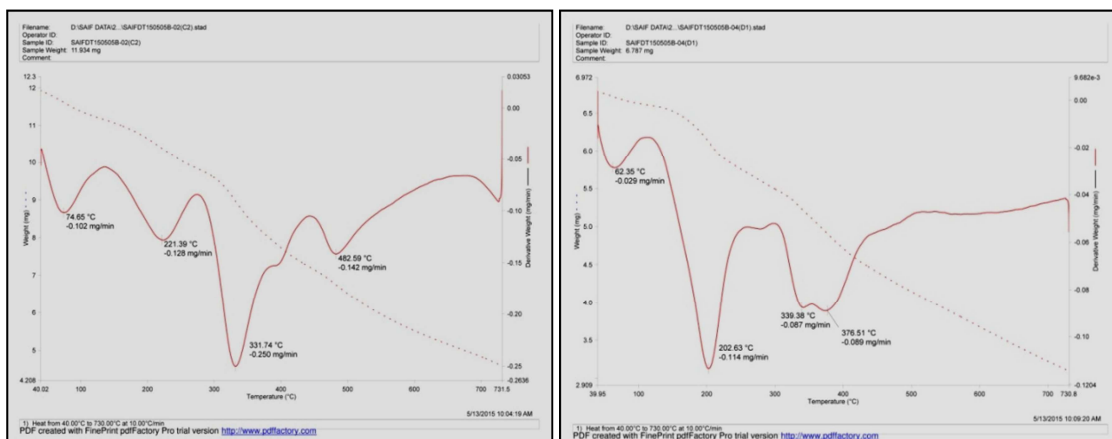
Code	I.R. Values (cm ⁻¹)								Electronic Spectra (nm)
	ν (OH) Free	ν (N=CH)	ν (C=N)	ν (C=N) ring	δ (N=CH)	γ (C=N)	ν (M-O)	ν (M-N)	
L1	3351	2836	1673	1599	1240	1069	-----	-----	500,230
1	3382	2971	1656	1597	1252	998	492	415	446,300,225
2	3346	2964	1539	1406	1127	954	490	410	690,510,230
3	3353	2978	1612	1531	1154	950	473	412	446,300,225
4	3337	2922	1618	1545	1101	1001	472	417	650,310,230
5	3375	2971	1649	1550	1259	1068	470	418	510,350

2.3 Thermal analysis

TGA data in the temperature range 40-300 $^{\circ}$ C is given in (Table 3). The loss of lattice water molecule occurs in all complexes below 100 $^{\circ}$ C. Loss of coordinated water in these complexes occurs in range 200-250 $^{\circ}$ C. In the case of Ni(II) complex, the weight loss corresponding to one lattice water and one coordinated water occurs continuously. Above 250 $^{\circ}$ C organic part of complexes begins to decompose Mn(II), Co(II) and Cu(II) complexes show two step decomposition while Ni(II) and Zn(II) complexes decompose in three steps.

Table 3 : Thermo gravimetric analysis data below 300 $^{\circ}$ C

Complex	Temperature	Weight Loss	Fragment	Nature of Fragment
	Range, $^{\circ}$ C	In mg	Loss	
[Mn(PIMQ)H ₂ O]H ₂ O	74.65	0.102	1H ₂ O	Lattice water
	221.39	0.12	1H ₂ O	Coordinated Water
[Co(PIMQ)(OAc)(H ₂ O) ₂]H ₂ O	62.35	0.02	1H ₂ O	Lattice water
	202	0.11	2 H ₂ O, 1OAc	Coordinated
[Ni(PIMQ)(H ₂ O)]H ₂ O	72.34	0.08	1H ₂ O	Lattice water
	210	0.1	1H ₂ O	Coordinated Water
[Cu(PIMQ)(H ₂ O)]	215	0.18	1H ₂ O	Coordinated Water
[Ni(PIMQ)(H ₂ O)]	250	0.16	1H ₂ O	Coordinated Water

TGA-DTA curve [Mn(PIMQ)H₂O]H₂O

and

[Co(PIMQ)(OAc)(H₂O)₂]H₂O

CONCLUSION

In this paper, coordination chemistry of 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol ligand described. The analysis confirmed the composition and structure of newly obtained complex combinations. From data it was observed that except Co (II) all complexes are having tetrahedral structure while Co (II) having octahedral structure. Ligand binds to metal at azomethine and pyridine N and phenolic OH of quinoxaline. It was observed that quinoxaline N did not take part in binding with metal.

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REFERENCES

- [1] Nagpal,P. and R.V Singh, *Appl. Organomet. Chem.*, **2004**, 18, 22-216.
- [2] Cheeseman G.W.H., Recent Advances in Quinoxaline chemistry, *Adv. Heterocycl. Chem.*, **1963**, 2, 203.
- [3] Torre M.H., Gambino D., Araujo D.J., Cerecetto H., Gonzalez M.,Lavaggi M.L., Azqueta M., De Cerain A.L., Vega A.M Abram U. and costa-Filno, *Eur.j. Med.chem.* **2005**, 40, 473.
- [4] Kim Y.B., Kim Y.H., Park J.Y and kim S.K Bioorg. *Med. Chem. lett.*, **2004**, 14, 541.
- [5] Schenfelder D. Slumm D., Bhola G., And Nicals N.J., *Pharmazie*, **1998**, 43, 837.
- [6] Paul F.F., Land S.A., Yang L. and Cufcik T., *J. Med. Chem.*, **1960**, 2, 973.
- [7] Sasee K., Wegle R., Unterslenhoefer and Grews G.F., *Angew. Chem.*, **1960**, 72, 973.
- [8] Refat M.S, EI-Deen I.M., Amoar z.m. and EI-Ghol S. *Coordi. Chem.*, **2009**, 62, 1702.
- [9] Wang P.H., Kck G.J., Lien E.J. and Lai M.C., *J. Med. Chem.*, **1990**, 608.
- [10] Ziegler J., Shurela T., Pasierb L., Klley C., Elamin A., Cole K.A., Wright D.W. *Inorga. Chem.*, **2000**, 39, 3731.
- [11] Chang D.W., K.S.J., Dai L. and Baek, *J. Synthetic Metals* **2012**, 162, 1196.
- [12]Mighani H. and Ghaemy M., *Chin. J. Polym. Science*, **2010**, 147.
- [13]Aldakov D., Palacious M. and Anzenbacher P. *Chem. Matter*, **2005**, 17, 5238.
- [14] Kozyrev A., Suresh V., Senge M., Dougherty T. and Pandey R., *Tetrahedron*, **2000**, 56, 3353.
- [15]Zarrouk A., Hammouti B., Touzani R., Al-Deyab s.s., Zertoubi M., Dafai A., and Elkadiris Inter. *J. Electrochem. Sciences.* **2011**,6,4939.
- [16]Hang T., Whang W., Shen J.Y., Wen Y., Ke T., Chen L. and Wu C., *Adv. Funct. Mater.* **2006**, 16, 1449.
- [17] Arvind K. Aghao, Dnyandeo M. Janrao, Siddharth Janrao , *Der Chemica Sinica*,**2015**,6(3) : 68-72.
- [18]W.J. Geary, *Coord.Chem. Rev.***1971**, 7, 81.
- [19]F.A. Cotton, G.Wilkinson, C.A. Murillo, M.Bochmann, *Advanced Inorganic Chemistry*, sixth edn. **1999** Wiley, New York.

[20] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. John Wiley and Sons, New York, **1986**.

[21] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, sixth edn. **1999** Wiley, New York.