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Chemistry

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF AZO DYE PYRIDINE-4-AMINE AND ITS METAL COMPLEXES

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ABSTRACT Metal(II) complexes have been synthesized with Schiff base azo dye ligand derived from condensation of (E)-4-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde and Pyridin-4-Amine Ligand (L3) and its metal complexes have been synthesized and characterized by elemental analysis, infrared spectra, 1HNMR, 13C NMR spectra, Molar conductance and magnetic susceptibility. The elemental analysis of the complexes confirm the stoichiometry of the type ML3 where, M=Cu(II), Ni(II), Co(II), and MLCl where M=Zn(II) Cd(II), Hg(II) and L= Schiff base. The Schiff base azo dye ligands and their metal complexes have been tested for their antimicrobial activity by MIC method.

KEYWORDS : Pyridine-4-Amine, Schiff base, Metal complexes, Spectral studies, Biological activity.

INTRODUCTION

Azo dyes are an important class of organic chemicals containing at least one azo chromophore (-N=N-) which donors the color for this famous type of dyes [1]. They play essential role in academic and applied research [2]. Electronic and geometrical features of azo metal dyes induce redox, nonlinear optical and magnetic properties and these properties lead to increase the sensitivity and stability of these compounds towards optical data storage device [3,4].

Azo dyes consider significant analytical reagents for the micro-estimation of metal ions. 1- (2-Pyridylazo)-2-naphthol considers well-known azo dye with term PAN which forms stable complexes with many metal elements2. In the same time, it is sensitive for trace concentration of metal elements and trace elements [5, 6]. This kind of complexes is highly colored therefore some of them used as dyes and pigments which leads to use it as inkjet printing and toner.

The azo dyes can be exhibited trans and cis isomers depending on the present –N=N– chromophore and these dyes can exhibit the photoisomerization process in their complexes[7]. The inter-conversion between the isomers can be achieved photo-chemically and it is possible thermally or electrochemically[8]. Trans isomer is more stable than cis isomer[9]. Azo dye ligands such as aryl azophenols have low-lying p* -orbitals which lead to stabilize the low valence metal redox state in their complexes by increasing chance of charge transfer transition of metal-to-ligand[10].

The drugs of pyridine such as sulfapyridine and salazosulfapyridine used as antiviral, antimicrobial, antioxidant as well as anti-malarial agents[11]. Sulfasalazine is azo dye of pyridine which called under the trade name Azulfidine in pharmacy. It widely employed for treatment of rheumatoid arthritis, Crohn's disease and ulcerative colitis[12,13]. Therefore, we hereby report to synthesis and characterization of azo dye of pyridine-4-amine and its synthesizing complexes and as well as screening their biological activity.

Tyre pile fires can burn for months, sending up an acrid black plume that can be seen for dozens of miles. That plume contains toxic chemicals and air pollutants, just as toxic chemicals are released into surrounding water supplies by oily runoff from Tyre fires. In order to prevent the environmental problem from growing, recycling Tyre is an innovative idea or way in this case. Recycling Tyre is the processes of recycling vehicles Tyres that are no longer suitable for use on vehicles due to wear or irreparable damage (such as punctures).

Tarun have reported that the compressive strength of rubberized concrete can be improve when fine aggregate was fully replaced by fine crumb rubber. He also indicated that if the rubberParticles have rougher surface or given a pretreatment, the better and improved bonding may develop with the surrounding matrix, and that may result in higher compressive strength.

Piti el outlined that crumb rubber responses were found to denote greater flexibility andToughness with larger deflection at peak load, longer post-peak load responses and higher fracture energy. Waste Tyres are a tremendous problem throughout the world. It is hardly surprising that in many countries it has been deduced that the best option is to simply burn them in cement kilns. At least in this way, the reasoning goes, some of the energy invested in the Tyre is reclaimed.

Experimental

All the chemicals used are of AR grade with a highest purity available. (E)-4-((2-fluorophenyl)dia-zenyl)-2-hydroxybenzaldehyde synthesized according to the literature procedure[14]. The metal and the chloride content were determined according to the procedure[15].

Synthesis of azo dye Ligand (L3)

5-((E)-(2-fluorophenyl)diazenyl)-2-((E)-(pyridin-4-ylimino)methyl)phenol

A mixture of (E)-4-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde (0.1 mol) and Pyridin-4-Amine (0.1 mol) in ethanol (30 ml) were refluxed on water bath for about 5-8 hrs. in presence of few drops of glacial acetic acid. The product which was separated out as crystalline solid on cooling was collected and recrystallized from ethanol. C18H13FN4O [L3]. Molecular Weight = 320.11, mp = 100°C, Yield= 64%.

Preparation of metal complexes: Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) with the Schiff base (L3).

Complexes were prepared by adding 10 ml of ethanolic metal salt (4 mmol) to an ethanol/chloroform (1:1 v/v) solution containing 8 mmol of the ligand (L3) and the mixture was refluxed for 6 hr. The obtained solution was left at room temperature and the resulting precipitates were filtered off, washed with ethanol and then recrystallized from ethanol / chloroform (1:3 v/v) solvent mixture.

Physical Measurements

All physical measurements, biological activity studies have been carried out as per the procedure given in the reference[16].

RESULTS AND DISCUSSION

Table – 1 Antimicrobial Activity

Compound Name	Zone of Inhibition (mm)											
	S. aureus			E. coli			A. Nizer			A. flavus		
mg/mL	25	50	100	25	50	100	25	50	100	25	50	100
L3	5	5	11	7	12	15	8	10	12	6	13	9
HTL3 Co	5	6	8	8	11	15	9	11	14	7	12	9
STL3 Cu	4	7	10	7	10	11	8	12	13	8	11	9
THL3 Ni	6	8	9	8	10	11	9	11	14	9	13	7
TTL3 Zn	5	6	11	7	11	15	8	10	12	7	11	12
HHL3 Hg	7	8	13	9	12	14	10	12	16	12	16	19
MNL3 Cd	7	9	12	9	13	15	11	12	16	12	17	20
Std II	08	10	15	10	14	18	12	13	18	14	18	23

The physical appearance and analytical results show that CuL3 Cl2 , CoL3 Cl2, NiL3 Cl2 and MLCl (Where M = Zn/Cd/Hg). The low molar conductance values (13.14 to 17.82 ohm-1 cm2 mol1) indicate the non-electrolytic nature of the complexes. All the complexes are light colored, stable and non-hygroscopic in nature having their melting points (<300 °C).

IR Studies

The IR spectra provided valuable information regarding the nature of functional group attached to the metal atom. The infrared spectral data of the Schiff base ligand show a medium intensity absorption band at 3418 cm–1 due to ν(O-H) stretching. Further the appearance sharp band at 1484 cm–1 indicate the presence of ν(N=N) stretching. Moreover, the appearance medium intensity band at 1672 cm–1 is, due to ν(C=N) a vibration of azomethine linkage. However, A broad absorption band is appeared at 3426 cm-1 in the IR spectra of the complexes of cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride due to the ν(O-H) stretching of associated water molecule. The ν(C=N) detected at 1619 cm–1 remains in same place in the case of metal complexes. Finally, the IR spectra of complexes exhibited new non-ligand bands in the range of 556–512 cm–1, 491–418 cm–1 and 391-343 cm–1 assigned as υ (M─O), υ (M─N) and υ (M─Cl) stretching vibrations, This result makes it clear that both "N" atoms of the ν(C=N) linkage are coordinated to a metal atom in chloride complexes[17,19].

Mass spectrum of azo ligand (L3)

The mass spectra of synthesized azo ligand (L3) Confirms the proposed formula by showing a molecular ion peak (m/z) at 325 (M+) which is slightly higher than the actual molecular weight of a azo ligand, showing the predicted structure.

Magnetic Properties

The cobalt complex exhibit magnetic moment value of 4.84 B.M. suggesting octahedral geometry. The Ni(II) complex show magnetic moment value of 2.87 B.M. slightly higher than spin only value (2.83 B.M), indicating an octahedral environment. The observed magnetic moment values for the Cu(II) complex are 1.88 suggesting a distorted octahedral geometry[20].

^{1}HNMR Spectral Studies

1HNMR spectra of the ligand shows signal at δ11.72 (s, -OH), and δ 10.32 (s, HC=N). This supports the formation of the Schiff base.

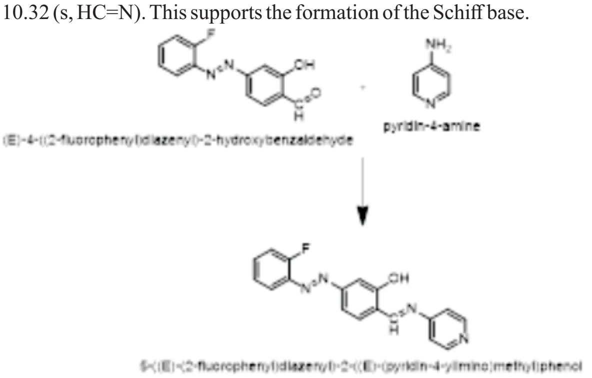

Figure 1: Synthesis of Ligand [L3]

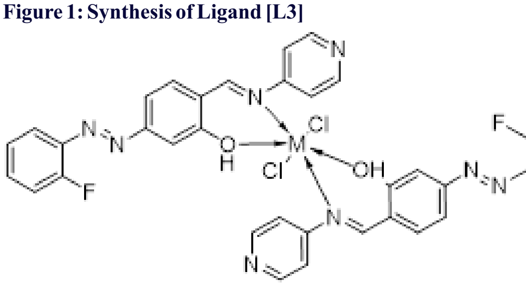

Figure 2: The Proposed Structure of Complexes

Antibacterial and Antifungal Analysis

The antibacterial activity of the Schiff base and its metal complexes were screened against the bacteria Escherichia coli, Staphylococcus aureus, Pseudomonas and antifungal activity of the synthesized compounds were screened against the Aspergillus niger, A Flavus species by MIC method at 100µg/mL, 50µg/mL, and 25µg/mL and concentrations. The results of the antibacterial and antifungal activities reveals that the values obtained by MIC method of Schiff base and its metal complexes showed that the complexes have higher growth inhibiting property than the Schiff base [21,22].

CONCLUSIONS

The formation of the compounds has been confirmed by the analytical data, IR, mass, 1H NMR, 13C NMR spectra, magnetic susceptibility and molar conductance data. The Schiff base acts as neutral bidentate coordinating through azomethine nitrogen and phenolic oxygen atoms to the metal ions. The antimicrobial activity results displayed that Cd(II) and Hg(II) complexes exhibit higher activity compared to Co(II), Ni(II) and Cu(II) complexes. On the basis of their analytical and spectral data, we propose octahedral geometry for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes (Figure-2).

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