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Synthesis, Characterization and Biological Aspects of O- and N-Donor Schiff Base Ligands and their Co(ll),Cu(ll),and Ni(ll) Complexes

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***Abstract*—** A Schiff base is a compound with the general structure $R_2C=NR'$. Schiff bases and their complexes are flexible compounds synthesized from the condensation of an amino compound with carbonyl compounds and extensively used for industrial purposes and also show a broad range of biological activities including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, anthelminthic and antipyretic properties. Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture. They can be considered a sub-class of imines. The term is often synonymous with azomethine which refers specifically to secondary aldimines.These are formed by the condensation reaction of primary ammines and carbonyl compounds. Furfuraldehyde and it′s various derivatives are also useful in the synthesis of Schiff bases. Schiff base forms a stable complex with metals in +2 oxidation state. Keeping all these facts into consideration, Here four new Complexes Co(ll),Zn(ll),Ni(ll) and Cu(ll) with O- and N- donor Schiff bases derived from Furfuraldehyde and Ethylenediamine have been synthesized and Characterized. In this chemical synthesis the ligands of schiff base was synthesized by the reaction of furfuraldehyde with Ethylenediammine in 2:1 ratio respectively in methanol. The analytical results and molecular weights of the compounds support the formulations. The obtained coloured crystalline Complexes are soluble in acetone and DMF but sparingly soluble in DMSO.

***Keywords*—** Azomethine; Biological activities; Condensation;DMF;DMSO; Furfuraldehyde; Synonymous

I. INTRODUCTION

Schiff bases and their complexes are flexible compounds synthesized from the condensation of an amino compound with carbonyl compounds and extensively used for industrial purposes and also show a broad range of biological activities including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, anthelminthic and antipyretic properties.[1] Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperatures.[2] The activity is usually increased by complexation therefore to understand the properties of both ligands and metal can lead to the synthesis of highly active compounds. The influence of certain metals on the biological activity of these compounds and their intrinsic chemical interest as multidentate ligands has prompted a considerable increase in the study of their coordination behavior[3]. Development of a new chemotherapeutic Schiff bases and their metal complexes is now attracting the attention of medicinal chemists. This review compiles the various synthesis procedures and application of Schiff bases and their metal complexe.Schiff bases and their transition metal complexes, containing nitrogen and oxygen donor atoms, play an important role in biological and inorganic research and have been studied extensively due to their unique coordination and biological properties[1,2.] Transition metal Schiff base complexes have found applications in various fields such as medicine, agriculture, industries etc. Furfuraldehyde is well known as an analytical reagent[4,5.] Its various derivatives6 are also useful.Cobalt forms very stable complexes with nitrogen donor ligands, both in the di- and tri-valent states, and both are thought to be implicated in the catalytic cation of the vitamin Zinc forms stable complexes in its invariable +2 oxidation state with ligands such as halides, CN- and those containing O, N and S donor atoms. In this chemical synthesis the ligands of schiff base was synthesized by the reaction of furfuraldehyde with Ethylenediammine in 2:1 ratio respectively in methanol.The reaction was refluxed on a water bath for 3-4 hours.the preciptates thereby obtained were separated and washed with methanol and were dried in a vaccum desicator.The crystals obtained are schiff base ligand.To form complexes ethanolic solution of schiff base and the metal salts of Cu(II),Ni(II),Zn(II) and Co(II) chlorides were made in 1:2 ratio.the solutions were refluxed for

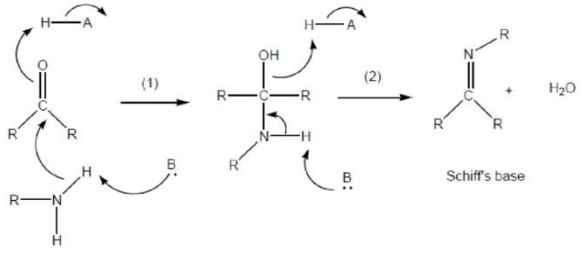
3-4 hours.Tthe resulting preciptates dried. Interest in the chemistry of Schiff bases and their metal complexes has increased in recent decades, because of the wide applications of these compounds in various fields[8]. Schiff bases have been shown to exhibit a broad range of biological activities, including antifungal,anticancer,antibacterial,antimalarial,anti-inflammatory,antiviral,antipyretic and herbicidal properties. However, the chelation of Schiff bases with transi- tion-metal ions was reported to improve the biological poten- tials of Schiff bases; hence, metal complexes of various Schiff bases are renowned as antibacterial, antifungal, anticancer, and antioxidant properties Metal complexes [Co(II),Cu(II) and Zn(II) ions] of Schiff base having played a central role in the development of co-ordination chemistry. Transition metal complexes have attracted curiosity due to DNA binding and cleavage properties under physiological conditions. Applications of metal complexes as chemical nucleases are the focus of current research[9] .It has been demonstrated that in-organic complexes as chemical nucleases are the focus of current research .It has been demonstrated that inorganic complexes can be used in foot printing studies as sequence specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research.

Rest of the paper is organized as follows, Section l contains the introduction of the schiff base Complexes and their biological activities, Section ll contains the related work done in the field of schiff base Complexes regarding their preparation, identification, detection and determination of their biological activities, Section lll contains the methodology of preparation of Schiff base and also describes the preparation of Co(ll),Zn(ll),Ni(ll) and Cu(ll) Complexes, Section lV contains the results obtained from all this experimental procedure and it also contains discussion regarding Schiff bases and their Complexes, Section V concludes the work with future directions.

II. RELATED WORK

Schiff bases are formed by the condensation of a primary amine with a carbonyl compound. Schiff bases of aliphatic aldehydes are relatively unstable and are readily polymerizable while those of aromatic aldehydes, having an effective conjugation system, are more stable.Schiff bases have number of applications viz., preparative use, identification, detection and determination of aldehydes or ketones,purification of carbonyl or amino compounds, or protection of these groups during complex or sensitive reactions Reaction with Primary Amines to form Imines. The reaction of aldehydes and ketones with ammonia or 1°-amines forms imine derivatives, also known as Schiff bases (compounds having a C=N function). Water is eliminated in the reaction, which is acid-catalyzed and reversible in the same sense as acetal formation.Jun 5, 2019.

Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine.The carbinolamine loses water by either acid or base catalyzed pathways.The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines. The end result of this reaction is a compound in which the C=O double bond is replaced by a C= The synthesis of a Schiff base from an aldehyde or a ketone is a reversible reaction and generally driven to completion by separation N double bond. This type of compound is known as an imine, or Schiff base. of the product or removal of water, or both. Preparation of Schiff bases under acidic conditions involves the following steps.



Equ 1: Mechanism of Schiff base Formation

III. METHODOLOGY

- **Method of Preparation**

All the chemicals and solvents used were of analytical grade. The metal salts $CoCl_2$.6H2O, ZnCl2 (Qualigens),CuCl2 and ZnCl2 available in pure state have been used as such. Furfuraldehyde obtained from Qualigens fine chemicals was distilled before use, whereas Ethylenediammine is used as received.

Synthesis of ligand(Schiff Base)

The ligands were synthesized by the reaction of furfuraldehyde with Ethylene in 1 : 1 or 2 : 1 molar ratio respectively in Methanol. The reaction mixtures were refluxed for 3-4 hrs. The precipitates thereby obtained were separated and washed with Mehanol and dried in oven

Synthesis of the Co (II) complex

To the hot methanolic solution (25 mL) of the ligand was added the hot methanolic solution (15 mL) of CoCl2.6H2O (0.001 mol) and the reaction mixrure was refluxed for 4-5 hrs. On cooling, the resulting coloured metal complexes precipitated out. The precipitates were washed with methanol.

Synthesis of the Zn (II) complex

The hot ethanolic solutions of ZnCl2 (0.001 mol) and schiff base (0.002 mol) were mixed and the mixture was refluxed for 4-5 hrs. The precipitates of the resulting metal complexes were filtered, washed with methanol.

Synthesis of Cu (II) Complex

The hot ethanolic solutions of CuCl2 (0.001 mol) and schiff base (0.002 mol) were mixed and the mixture was refluxed for 4-5 hrs. The precipitates of the resulting metal complexes were filtered, washed with methanol.

Synthesis of Ni (ll) Complex

The hot ethanolic solutions of NiCl2 (0.001 mol) and schiff base (0.002 mol) were mixed and the mixture was refluxed for 4-5 hrs. The precipitates of the resulting metal complexes were filtered, washed with methanol.

IV. RESULTS AND DISCUSSION

PHYSICAL PROPERTIES

The reactions of complexes with schiff bases have been carried out in unimolar and bimolar ratios in ethanol.The analytical results and molecular weights of the compounds suppot the formulations represented in the table 1.All the Complexes are coloured, crystalline powders and are soluble in acetone,DMF but sparingly soluble in DMSO.
Some of the physical properties of these Complexes are demonstrated in the table below.

Table 1: physical Characterization

Complex	Colour	M.P °C	F.wt g/mol	%age yield
$[Co(SB)_2Cl_2]$	Dirty green	120	471.5	63.68
$[Cu(SB)_2Cl_2]$	Dark purple	241	425.93	74.11
$[Zn(SB)_2Cl_2]$	Lemon yellow	243	409.75	72.75
$[Ni(SB)_2Cl_2]$	Reddish brown	240	242.17	65.94

- Here (SB) is Schiff base**.**

IR Spectral studies

The IR spectra of the ligands showed (Table 2) a band in the range 1647-1635 cm-1, which is due to ν(C=N). This band shifts to lower frequency 1640-1620 cm-1 in all the Co (II) and Zn (II) complexes possibly indicating the coordination to metal ions through the azomethine nitrogen9, 10. The C-O-C band appeared at 1150 or 1148 cm-1 in the spectra of SB1 or SB2, respectively, shifted to 1140-1120 cm-1 in the spectra of the complexes. Such a shifting is probably due to the involvement of furfural ring oxygen in coordination11. Two distinct bands appeared in the region 468-434 cm-1 and 592-548 cm-1 in the spectra of complexes are due to ν(M-N) and ν(M-O), respectively and these further provide evidence for the coordinated metal ion in the ligand framework.

Discussion

The schiff base was formed by by the reaction of furfuraldehyde and Ethylenediammine.The colour of he resulting comples was changed from that of the parent compounds this indicated the formation of some new compound which was later on confirmed measuring its solublity.The resulting compound was insoluble in the solvent methanol and was partially soluble in the inorganic solvents. The IR studies also provide the evidence of the formation of the schiff base.The peakes of C=O which shows peakes at 1500-1650cm- in the IR spectrum were disappeared when the IR spectra of the resulting compound was taken again.New peakes of of carbon nitrogen double at 1750cm- .this shows that the resulting schiff base was formed.The reactions of CoCl2.6H2O or ZnCl2 with the Schiff bases have been carried out in unimolar and bimolar ratios in ethanol. The analytical results and molecular weights of the compounds support the formulations represented in Table 1. All the complexes are coloured, crystalline powders and are soluble in acetone and DMF but sparingly soluble in DMSO.Different techniques have been used to confirm the formation of the schiff base and the resulting metal complexes which have wide spread antibacterial and biological activities.All the theoratical and experimental data supported the formation of schiff base and its complexes with the transition metals having oxidation state of +2.

Applications of schiff base Imine complexes

They have a broad range of biological properties: antitumor, antiviral, antifungal, antibacterial [10].They are also used in the treatment for diabetes and AIDS. As biological models, they help in understanding the structure of biomolecules and biological processes occurring in living organisms. They participate, inter alia, in photosynthesis and oxygen transport in organisms. They are involved in the treatment of cancer drug resistance, and often tested as antimalarials. It also could be used for the immobilization of enzymes [11, 12].

Biological Activity

Schiff bases are characterized by an imine group −N=CH-, which helps to clarify the mechanism of transamination and racemization reaction in biological system [1]. It exhibits antibacterial and antifungal effect in their biological properties [13, 14]. Metal-imine complexes have been widely investigated due to antitumor and herbicidal use. They can work as models for biologically important species [13].

Antibacterial properties

Mortality increase caused by infectious diseases is directly related to the bacteria that have multiple resistance to antibiotics. The development of new

antibacterial drugs enriched by innovatory and more effective mechanisms of action is clearly an urgent medical need [15]. Schiff bases are identified as promising antibacterial agents. For example, N-(Salicylidene)-2-hydroxyaniline iis active against Mycobacterium tuberculosis [4].

Antifungal properties

Fungal infections usually are not only limited to the contamination of surface tissues. Recently, there was a considerable increase in the incidence of systemic fungal infections, which are potentially lifethreatening [17]. Exploration and development of more effective antifungal agents is necessity, and the individual Schiff bases are considered to be promising antifungal medicines [18].Antifungal properties Some of them, such as imine derivatives of quinazolinones possess antifungal properties against Candida albicans, Trichophyton rubrum, T. mentagrophytes, Aspergillus niger and Microsporum gypseum. Schiff bases and their metal complexes formed between furan or furylglycoxal with various amines exhibit antifungal activity against Helminthosporium gramineum − causing leaf stripe in barley, Syncephalostrum racemosus − contributing to fruit rot in tomato and Colletotrichum capsicum causing anthracnose in chillies[7]

Biocidal properties

Schiff bases obtained by the synthesis of o-aminobenzoic acid and β-keto esters have found biocidal use against S. epidermidis, E. coli, B. cinerea and A. niger [2]. By contrast, Schiff bases of isatin derivatives are used in the destruction of protozoa and parasites.

Metal complex in neurological disorders

Metal complexes also play a vital role in the treatment of various neurological disorders. These complexes may cure many nerve disorders like Huntington′s chorea, Parkinsonism, organic brain disorder, epilepsy and paralysis. Transition metals such as copper and zinc are involved as a transmitter in the neuronal signaling pathways.

Metal complexes in diabeties

Some metal complexes show considerable reduction in the glucose levels e.g. intake of chromium metal complex. Insulinomimetic Zinc complex with different coordination structures and with a blood glucose lowering effect is reported to treat type 2 diabete.

Antitumor and Cytotoxic Activities

Interaction of DNA with transition metal complexes has gained considerable current interest due to its various applications in cancer research and nucleic acid chemistry. To understand clearly the binding behavior of DNA with Schiff base metal complexes, a brief description about structure of DNA, its binding modes and cleavage is given below. 8) Antiviral properties The use of vaccines may lead to the eradication of pathogens known viruses, such as smallpox, poliomyelitis (polio), whether rubella. Although there are many therapeutic ways to work against viral infections, currently available antiviral agents are not fully effective, which is likely to cause a high rate of mutation of viruses and the possibility of side effects. Salicylaldehyde Schiff bases derived from 1-amino-3-hydroxyguanidine tosylate are good material for the design of new antiviral agents [4]. Isatin Schiff base ligands are marked by antiviral activity, and this fact is very useful in the treatment of HIV. In addition, it was also found that these compounds have anticonvulsant activity and may be included in the anti-epileptic drugs. Gossypol derivatives also present high antiviral activity. Increasingly, gossypol, often used in medical therapy is replaced by its derivatives, because of their much lower toxicity. Schiff bases have obtained acceptable results for Cucumber mosaic virus, whose effectiveness was estimated at 74.7% [7].

Antimalarial properties

Malaria is a disease which when is neglected causes serious health problems. Human malaria is largely caused by four species of the genus Plasmodium (P. falciparum, P. vivax, P. ovale and P. malariae). The search for new drugs, vaccines and insecticides for the prevention or treatment of this disease is a priority. Schiff bases are interesting compounds, which could be part of antimalarial drugs. For example, the compound with such effect is Ancistrocladidine , which is a secondary metabolite produced by plants of the family Ancistroscladaceae and Dioncophyllaceae, and presenting an imine group in a molecular chain [4]

Application in modern technologies

Photo- and thermochromic properties of Schiff bases as well as their biological activity make them applicable in modern technology. Among others, they are used in optical computers, to measure and control the intensity of the radiation, in imaging systems, as well as in the molecular memory storage, as organic materials in reversible optical memories and photodetectors in biological systems. Due to photochromic properties, Schiff compounds could behave as photostabilizers, dyes for solar collectors, solar filters. They are also exerted in optical sound recording technology. Among others, worthy of interest in the properties associated with Schiff rules include: properties of liquid crystal chelating ability thermal stability optical nonlinearity and the ability to create the structure of a new type of molecular conductors using electrical properties to proton transfer . Because of its thermal stability Schiff bases can be used as stationery phase in gas

chromatography. The optical nonlinearity of these compounds allows us to use them as electronic materials, opto-electronic (in optical switches) and photonic ccomponent. Imine derivatives can be exerted to obtain conductive polymers. Schiff bases as an electrical conductor possess a variety range of uses: as catalysts in photoelectrochemical processes, electrode materials and micro-electronic equipment, organic batteries or electrochromic display device (graphical output devices) [7]. Due to the presence of the imine group, the electron cloud of the aromatic ring and electronegative nitrogen, oxygen and sulfur atoms in the Schiff bases molecules, these compounds effectively prevent corrosion of mild steel, copper, aluminium and zinc in acidic medium.

V. CONCLUSION AND FUTURE SCOPE

Schiff bases and their complexes are flexible compounds synthesized from the condensation of an amino compound with carbonyl compounds and extensively used for industrial purposes and also show a broad range of biological activities including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, anthelminthic and antipyretic properties. Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture.We have synthesized and characterized four new complexes of Co (II),Zn (II),Ni(II) and Cu(II) with O- and N-donor Schiff bases derived from Furfuraldehyde and Ethylenediammine.In this chemical synthesis the ligands of schiff base was synthesized by the reaction of furfuraldehyde with Ethylenediammine in 2:1 ratio respectively in methanol.The reaction was refluxed on a water bath for 3-4 hours.the preciptates thereby obtained were separated and washed with methanol and four complexes were made from the resulting schiff base ligand.The ligands and their metal complexes have been characterized on the basis of IR studies.Schiff bases and their transition metal complexes, containing nitrogen and oxygen donor atoms, play an important role in biological and inorganic research and have been studied extensively due to their unique coordination and biological properties1,2. Transition metal Schiff base complexes have found applications in various fields such as medicine, agriculture, industries3 etc. Furfuraldehyde is well known as an analytical reagent4,5. Their derivatives are also useful in various biological and antibacterial activities.

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