



RESEARCH ARTICLE

ANTI-MICROBIAL STUDIES OF NEWLY SYNTHESIZED TRANSITION METAL COMPLEXES USING SCHIFFBASE LIGAND (E)-N²-(FURAN-2-YLMETHYLENE) PYRIDINE-2, 6-DIAMINE

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ABSTRACT

Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compounds and widely used for industrial purposes and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Development of a new chemotherapeutic Schiff bases and their metal complexes is now attracting the attention of medicinal chemists. A novel schiffbase ligand is synthesized by aldehyde with Aromatic Amine to form Schiffbase ligand (L). It is mixed with 1stRow transition metal ions to form metal complexes. Complexes are characterized by Elemental analysis, UV- spectroscopy, Infrared spectroscopy and NMR. Elemental analysis of the metal complexes was suggested that the stoichiometry ratio is 1:2 (metal-ligand). The UVspectrum gives clear idea about the metal complexes. The Schiff base complexes have been screened for their invitro antibacterial activity against three bacteria via; (Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus sp.) also studied antifungal activities (Aspergillus Niger and Aspergillus flavus). Anti-oxidant properties of metal complexes also have been studied.

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INTRODUCTION

A Schiff base is a compound formed from the condensation of either an aldehyde or a ketone (Holm *et al.*, 1966; Hobday and Smith, 1972; Pierre, 1987). The carbonyl group of the aldehyde gives aldimines while that of ketone givesketoimines. It has been known that different metal ions on interaction with Schiff bases yield chelates, for example Tsumaki, (1983) reported [Co(sal2-en)] Complex which received a great attention owing to its ability to undergo reversible adduct formation with molecular oxygen. The oxygenation ability of the complex was first recognized by Hassan *et al*, (1998). Schiff bases have been playing an important part in the development of Co-ordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. They play an important role in both synthetic and structural research, because of their preparative accessibility and structural diversity. Schiff base compounds as ligands have gained importance because of the physiological andpharmacological activities associated with them.

They constitute an interesting class of chelating agents capable of coordination with metal ions given complex which serve as models for Biological system (Yang, 2002 and Singh, 2010). The tetradentative Schiff base metal complexes are one of the most well-known complexes, since the ligands can be easily synthesized. These metal complexes are stable and have many applications, such as catalysis and as O₂-storage devices (Parshall, 1992 and Chantarasiri, 2000). Schiff bases as tetradentate ligands coordinate predominantly in a planar arrangement to various metal ions giving trans geometries in octahedral complexes, metal complexes of tetradentative salicylaldimine ligands had until relatively recently only been formed with trans geometry. Three new metal complexes of Cr(III), Pb(II) and TiO(IV) ions with a Schiff base derived from salicylaldehyde and urea have been investigated. The present work investigates the synthesis and properties of new tetradentative Schiff base ligand containing ether moiety with Cr(III), Co(II), Ni(II), Cu(II) and Cd(II) ions and characterize their geometrical structures by using different physical techniques. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications (Taylor, 2004 and Yamada, 1999). The interest in the design, synthesis and characterization of the transition metal complexes of unsymmetrical Schiff base ligands hascome from the realization that coordinated ligands around central metal ions

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in natural systems are unsymmetrical. Recently, this class of compounds has also attracted much attention in the field of optoelectronic technologies for their large nonlinear responses (Khandar, 2002). In the area of the bioinorganic chemistry, interest in the Schiff base complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and enzymes (Al-Shihri, 2004; Kovbasyuk, 1997 and Gupta, 2002). They appear to be of importance for a broad range of transition metal catalyzed reactions including lactidepolymerization (Bu, 2003 and Dasm, 1995), epoxidation of olefins (Atwood, 2001) and hydroxylation (Cozzi, 2004).

Several reviews have been published on metal Schiff bases especially on metal Salen Schiff base complexes (Dixon, 1975 and Karplus, 1997). Unsymmetrical Schiff base ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the composition and the geometry of the metal ion binding sites in the metallo-proteins and the enzymes, and the selectivity of the natural systems with synthetic materials (Li, 2007). The aminooxidase enzyme requires such a coenzyme besides copper(II) ions for catalytic activity. Urease, the first enzyme crystallized to be shown to possess nickel ions (Asadi, 2007), is an important enzyme in both agriculture and medicine, which rapidly catalyzes the hydrolysis of urea to form ammonia and carbamic acid (Asadi, 2008). Recently Cu(II) and Ni(II) Schiff base complexes have been investigated as inhibitor against urease and xanthine oxidase (XO) (Asadi, 2009). Inorganic elements play crucial role in biological and bio-medical Processes, and it is evident that many organic compounds used in medicine do not have a purely organic mode of action, some are activated or bio transformed by metal ions metabolism. Many drugs possess modified toxicological and pharmacological properties in the form of metal complex and probably Schiff bases are versatile $-C=N-H$ (Imine) containing compounds possessing broad spectrum of biological activity and incorporation of metals in form of complexes showed some degree of antibacterial, antifungal, antitumor and anti-inflammatory activity. In Schiff base azomethane nitrogen and other donor atoms like oxygen play a vital role in co-ordination chemistry. Hence an attempt is made to study the interaction of reduced Schiff base with transition metals of biological interest and to investigate the co-ordination chemistry of such interactions. In the present work we described the synthesis and characterization of reduced Schiff base and its metal complexes. Moreover antibacterial and antifungal activity of reduced Schiff base metal complexes is also evaluated and compared with the standards.

Aromatic aldehydes especially with an effective conjugation system, form stable Schiff bases, whereas those aliphatic aldehydes are unstable and readily polymerize. Schiff base ligands with aldehydes are formed more readily than with ketone (carbonyl carbon). Schiff base have very flexible and different structures. A wide range of Schiff base compounds and their behavior studied because these compounds have very flexible and diverse structure. Schiff bases are generally are bi, tri, or tetra-dentate chelate ligands and form very stable complexes with them. Their chemical and physical properties in various fields such as preparative uses, identification, or protection and determination of aldehyde or ketone. Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes,

because Schiff base complexes are potentially capable of forming stable complexes with metal ions. Many Schiff base complexes show excellent catalytic activity in various reaction at high temperature and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes. Metal complexes of Schiff base having played a central role in the development of coordination 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. It has been demonstrated that inorganic complexes as chemical nucleases are the focus of current research. It has been demonstrated that inorganic complexes can be used in footprinting studies as sequence specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research.

Schiff bases have a large number of synthetic uses in organic chemistry. Acylation of Schiff bases by acid anhydrides, acid chlorides and acyl cyanides is initiated by attack at the nitrogen atom and leads to net addition of the acylation agent to the carbon-nitrogen double bond. Reactions of this type have been put to good use in natural product synthesis. Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate. One of the most important types of catalytic mechanism is the biochemical process which involves the condensation of a primary amine in an enzyme usually that of a lysine residue, with a carbonyl group of the substrate to form an imine, or Schiff base. Early time the severe infectious diseases caused by gram positive and gram negative pathogenic bacteria inflated to threat level around the world. This increase as well as emergence of bacteria immune to ordinarily used antibiotics has resulted in the need to develop new categories of antibacterial agents to combat infections. The chemistry of biological science has produced a number of compounds that are now employed as antibacterial agents. Such type compounds revealed great promise in this area is the Schiff base. Schiff base also known as imine or azomethine, named after Hugo Schiff was reported in 19th century by Schiff (1864). The classical synthesis with a carbonyl compound. The most commonly used method of obtaining Schiff base is by the condensation reaction Figure-1.

The Schiff base compound with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group not a hydrogen^[26]. Schiff bases in broad sense have the general formula $R_1 R_2 C=N R_3$, Where R is an organic side chain. Some restrict the term to the secondary aldimines (azomethine where the carbon is connected to a hydrogen atom), thus with the general formula $RCH=NR$. Schiff bases with thiophene carboxaldehyde and aminobenzoic acid show anti-bacterial activity. Lysine based Schiff bases and their complexes with La, Co, Fe, show bacteriostatic activity to *B. subtilis*, *E. coli* and *S. aureus*. Zn (II), Cd (II), Ni(II), and Cu(II) complexes with furfural and semicarbazide, and with furfurylidene diamine. Schiff bases show antibacterial activities. Organo-silicon (IV) complexes with bidentate Schiff bases, organo-lead (IV) complexes with nitrogen donor ligands of sulphur drugs possess antibacterial activities.

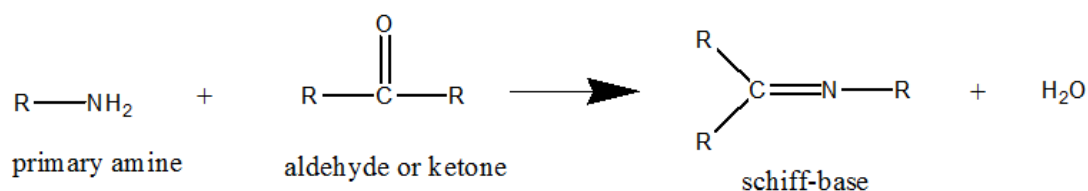


Figure 1. The most common method for synthesizing a Schiff base

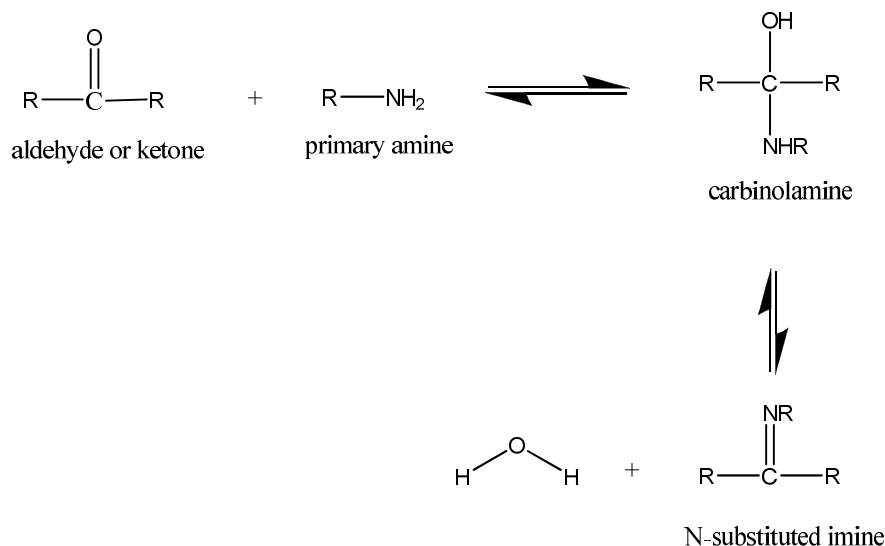


Figure 2.

Schiff base derived from 2-thiophenecarboxaldehyde and 2-chlorophenyl hydrazine. Tentative structures have been proposed on the basis of analytical, spectral, magnetic, and conductance data. In order to establish a modern technique to prepare some of Nano metricoxide using Schiff base compounds and collected the biological role of metals, this prepared Schiff base and its metal chelates have been screened for biological activity against some kind of bacterial (G⁺ and G⁻) and fungi. The synthesis of metal oxide nano particle has received considerable attention with their potential applications in various fields.

Several varieties of nano particles with biomedical relevance are available including, polymeric nano particles, metal nano particles. It is also known that mono and bishydrazones find wide application in medicine as active physiological preparations, due to their antibacterial, tuberculostatic, fungicidal properties, as well as activities against certain types of cancers and microorganisms. Benzylidene derivatives have also found wide application, not only because of their strong activity against some microorganisms, but also because they can act as free radical scavengers. Many coordination compounds of transition metals with Schiff bases greater activity than the ligands alone.

Mechanism

The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating. The formation is generally driven to the completion by separation of the product or removal of water, or both. Many Schiff base can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.

Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophile, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases synthesis are best carried out at mild acidic pH.

The dehydration of carbinolamine is also catalyzed by base. This reaction is somewhat analogous to the E₂ elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate. The Schiff base formation is really a sequence of two types of reactions, i.e. addition followed by elimination. The mechanism of Schiff base formation is another variation on the theme of nucleophile addition to the carbonyl group. In this case, the nucleophile is the amine. 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. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration.

Biological importance

Stereo chemical investigation carried out with the aid of molecular model showed that Schiff base formed between methylglyoxal and the amino group of the lysine side chains of proteins can bent back in such a way towards the N atom of peptide groups that a charge transfer can occur between these groups and oxygen atoms of the Schiff bases. In this respect pyridoxalSchiff bases derived from pyridoxal and amino acids have been prepared and studied from the biological point of view. Several studies have revealed that by condensation of salicylaldehyde with different heterocyclic compound and their derivative with potent antibacterial and antifungal activity obtained.

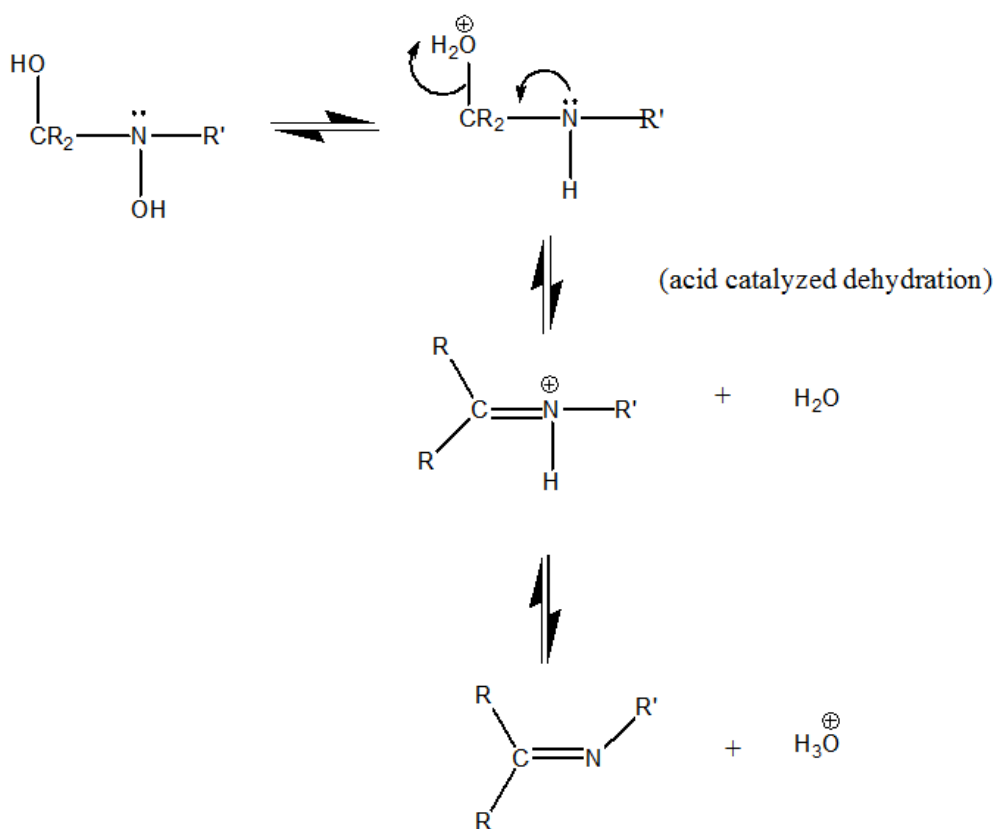


Figure 3.

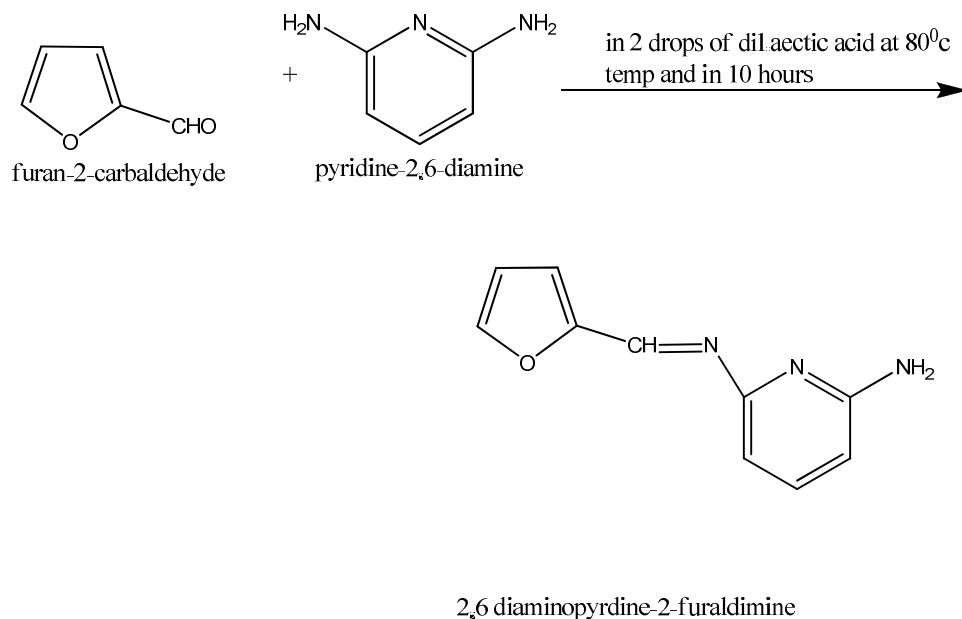
Osman prepared thiadizole derivative compound of salicylaldehyde which were found to be highly potent antibacterial against *Bacillus cereus* and antifungal against *Aspergillus niger*. Several compound incorporating piperazinyguanidine when condensed with Salicylaldehyde were found to exhibit cardiovascular and vasodepressive antimicrobial activity.

Application in Biochemistry: Schiff bases are common enzymatic intermediates where an amine, such as the terminal group of a lysine residue reversibly reacts with an aldehyde or ketone of a cofactor or substrate. The common enzyme cofactor PLP forms of a Schiff base with a lysine residue and is transaldiminated to the substrate. Similarly, the cofactor retinal forms a Schiff base in rhodopsin, including human rhodopsin (via Lysine 296), which is key in the photoreception mechanism.

An example where the substrate forms a Schiff base to the enzyme is the fructose 1,6-bisphosphate aldoses catalyzed reaction during glycolysis and in the metabolism of amino acids. A number of drugs contain metals. This theme relies on the study of the design and mechanism of action of metal-containing pharmaceuticals, and compounds that interact with endogenous metal ions in enzyme active sites. The most widely used anti-cancer drug is cisplatin. MRI contrast agent commonly contain Gadolinium. Lithium carbonate has been used to treat the manic phase of bipolar disorder. Gold antiarthritic drugs, e.g. auranofin have been commercialized. Carbon monoxide-releasing molecules are metal complexes have been developed to suppress inflammation by releasing small amounts of carbon monoxide. The cardiovascular and neuronal importance of nitric oxide has been examined, including the enzyme nitric oxide synthase.

Biological importance of Copper: Copper-alloy touch surfaces have natural intrinsic properties to destroy a wide range of microorganisms (e.g., *E. coli* O157:H7, methicillin-resistant *Staphylococcus aureus* (MRSA), *Staphylococcus*, *Clostridium difficile*, influenza A virus, adenovirus, and fungi). Some 355 copper alloys were proven to kill more than 99.9% of disease-causing bacteria within just two hours when cleaned regularly. The United States Environmental Protection Agency (EPA) has approved the registrations of these copper alloys as "antimicrobial materials with public health benefits," which allows manufacturers to legally make claims as to the positive public health benefits of products made with registered antimicrobial copper alloys. In addition, the EPA has approved a long list of antimicrobial copper products made from these alloys, such as bedrails, handrails, over-bed tables, sinks, faucets, door knobs, toilet hardware, computer keyboards, health club equipment, shopping cart handles, etc. (for a comprehensive list of products, see: Antimicrobial copper-alloy touch surfaces Approved products). Copper doorknobs are used by hospitals to reduce the transfer of disease, and Legionnaires' disease is suppressed by copper tubing in plumbing systems. Antimicrobial copper alloy products are now being installed in healthcare facilities in the U.K., Ireland, Japan, Korea, France, Denmark, and Brazil^[citation needed] and in the subway transit system in Santiago, Chile, where copper-zinc alloy handrails will be installed in some 30 stations between 2011–2014.

Biological importance of Nickel: Although not recognized until the 1970s, nickel plays important roles in the biology of microorganisms and plants. The plant enzyme urease (an enzyme that assists in the hydrolysis of urea) contains nickel. The NiFe-hydrogenases contain nickel in addition to iron-sulfur clusters.



Scheme 1. Synthesis of Ligand

Such [NiFe]-hydrogenases characteristically oxidize H₂. A nickel-tetrapyrrole coenzyme, Cofactor F430, is present in the methyl coenzyme M reductase, which powers methanogenic archaea. One of the carbon monoxide dehydrogenase enzymes consists of an Fe-Ni-S cluster. Other nickel-containing enzymes include a rare bacterial class of superoxide dismutase and glyoxalase I enzymes in bacteria and several parasitic eukaryotic trypanosomal parasites (this enzyme in higher organisms, including yeast and mammals, uses divalent zinc, Zn²⁺). Nickel can have an impact on human health through infectious diseases arising from nickel-dependent bacteria. Nickel released from Siberian Traps volcanic eruptions (site of the modern city of Norilsk) is suspected of having had a significant impact on the role played by Methanosarcina, a genus of euryarchaeote archaea that produced methane during the biggest extinction event on record.

Biological importance of Vanadium: Vanadium plays a limited role in human biology. It is more important in marine environments than terrestrial active site of the enzyme vanadium bromoperoxidase, which produces the preponderance of naturally-occurring organobromine compounds.

Experimental Work

The experimental work mainly concerns on the synthesis of (2,6-diamino pyridine-2-furaldimine)(L) and its synthesis of metal complexes of Cu(II), Ni(II), V(V)

CHEMICALS

- 2,6-diamino pyridine
- 2-Furaldehyde
- Dil. Acetic acid
- Ethanol

Synthesis of Ligand: The Aromatic aldehyde/substituted aldehyde in ethanol (20mmol) are mixed with 20mmol of Amine/substituted amine, and the mixture is stirred for 1-2 hours for the magnetic stirrer method.

Synthesis of 2,6-diamino pyridine-2-furaldimine (L): A Solution of 2-Furaldehyde was added to 2,6-diamino pyridine in 20 ml alcohol and 2 drops of dil. Acetic acid was added. The mixture was refluxed for about 10 hours. The mixture was cooled in ice. The resulting precipitate was then filtered, washed with ethanol and dried. The product was recrystallization from hot ethanol gave (L).

Synthesis of metal complexes

To an ethanolic solution of the Schiff Base Ligand and the solution of metal (Copper acetate (II), Nickel Sulphate(II), Vanadium pentoxide(V)) was added in a molar ratio (1:2). The mixture was refluxed for about 2 hours. The mixture was cooled in ice. The resulting precipitate was collected by filtration, washed with ethanol and dried. Crystallization from aqueous ethanol gave pure crystals of metal complexes.

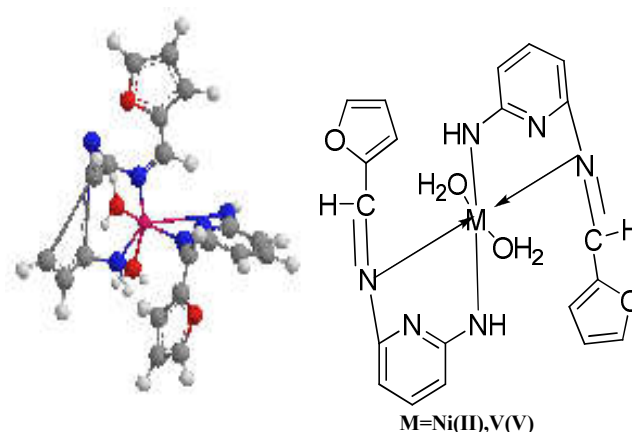
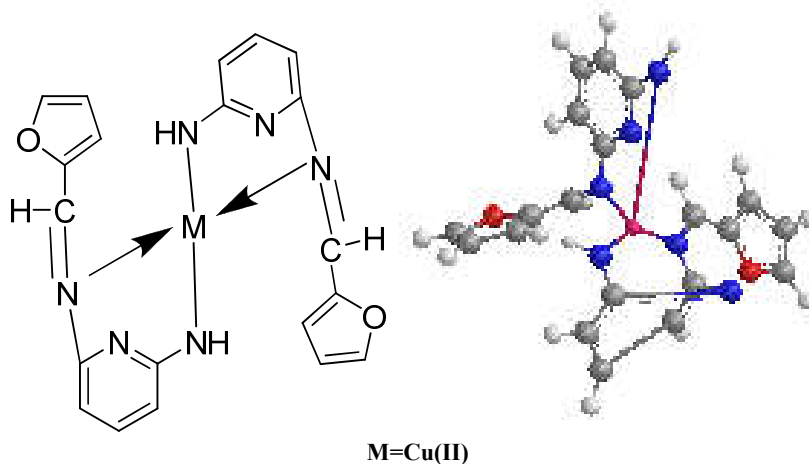


Figure 4. Octahedral geometry of Nickel and vanadium complexes and molecular modeling

Spectral Characterization

UV-Visible Spectra: The UV visible electronic spectra (200-800nm) were recorded by UV-Vis-1800 series (Shimadzu) double beam spectrophotometer using DMSO solvent.



M=Cu(II)
Figure 5. Tetrahedral geometry of copper complex and molecular modeling

Table 1 Elemental Analysis of ligand and complexes

Compounds	Physical appearance	Melting point (°C)	Elemental (%) Calc.(found)					m/z
			C	H	N	O	M (metal)	
Ligand (L)	Black	300	64.16 (64.12)	4.85 (4.84)	22.45 (22.43)	8.55 (8.52)	–	187.07
Cu - L	Green	320	56.06 (56.05)	4.03 (4.02)	18.68 (5.46)	7.11 (7.13)	14.12 (14.11)	449.08
V - L	Yellow	310	53.28 (53.25)	4.68 (4.69)	17.75 (17.76)	13.52 (13.50)	10.76 (10.79)	473.11
Ni - L	Red	300	52.42 (52.40)	4.61 (4.63)	17.75 (17.74)	13.52 (13.50)	10.76 (10.78)	473.11

The electronic absorption spectra of the Schiff base and its metal complexes were recorded at room temperature.

FT-IR spectra: FT-IR spectra were recorded using KBr pellets in Shimadzu FT-IR 8201 spectrometer (4000-400 cm^{-1}).

NMR spectra: The ^1H -NMR spectra of Schiff base ligand is recorded in CDCl_3 solution using tetramethylsilane (TMS) as an internal standard and temperature at 300°C. It is operated in Bruker Analytics Instrument.

ANTI MICROBIAL STUDIES

Antibacterial activity of compounds against bacterial pathogens using Well diffusion method: Antibacterial activity of the extract of compounds was determined using well diffusion method (Gamet, 2006). It was performed by sterilizing Muller Hinton agar media. After solidification, wells were cut on the Muller Hinton agar using cork borer. The test bacterial pathogens were swabbed onto the surface of Muller Hinton agar plates. Wells were impregnated with 25 μl of the test samples. The plates were incubated for 30 min to allow the extract to diffuse into the medium. The plates were incubated at 30°C for 24 hrs, and then the diameters of the zone of inhibition were measured in millimeters. Each antibacterial assay was performed in triplicate and mean values were reported.

Antifungal activity of Ligand and its complexes against fungal pathogens using well diffusion method: Antifungal activity of the extract of compounds was determined using well diffusion method. Similar procedure was carried out here also.

Anti-Oxidant studies: It is well documented that reactive oxygen species (ROS) are involved in the etiopathogenesis of numerous chronic diseases such as atherosclerosis,

hypertension and coronary heart disease (Earnshaw, 1968). These free radicals are produced under certain environmental conditions and during normal cellular functions in the body. Antioxidants thus play an important role to protect the human body against damage by reactive oxygen species. The ability of Schiff bases and their metal complexes to scavenge free radicals is an important property. Different modes of action such as being free radical terminators, chelators of metal ions involved in catalyzing lipid oxidation or an oxygen scavenger that reacts with oxygen closed systems have been used in categorizing antioxidants (Sathya, 2017). In this study, we present the DPPH scavenging ability of the Schiff base and the corresponding Ni (II), Cu (II) and V (II) complexes. The antioxidant assay was carried out using different concentrations of the test samples, while ascorbic acid (vitamin-C), rutin and butylated hydroxytoluene (BHT) were used as standards.

RESULT AND DISCUSSION

The metal complexes are insoluble in water and soluble in DMSO, DMF, CHCl_3 and acetone, slightly soluble in methanol and ethanol. The physical properties of the ligand and complexes are presented in Table 1.

Elemental Analysis

The micro-elemental analysis for C, H, N and S as well as the molecular weight of the complexes obtained were in agreement with the predicted formula for complexes.

FT-IR Spectra: Infra-red spectrum is an important record which gives sufficient information about the structure of a compound. Unlike ultraviolet spectrum which comprises of relatively few peaks, this technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound.

Table 2. UV-Spectra for ligand and its metal complexes

Compounds	Frequency		ϵ_{\max}	Transition	Geometry
	Nm	cm^{-1}			
Ligand	273.00	36630.04	-	$\pi \rightarrow \pi^*$	-
	210.50	47619.05	-	$n \rightarrow \pi^*$	-
Cu(II)- complex	656.00	15243.90	10^3	${}^2B_{1g} \rightarrow {}^2B_{2g}$	Tetrahedral
	598.50	16708.44	10^3	${}^2B_{1g} \rightarrow {}^2A_{1g}$	
Ni(II)-complex	274.50	36429.87	10^3	$\pi \rightarrow \pi^*$	Octahedral
	275.50	36297.64	10^2	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
V(V)-complex	211.50	47281.32	10^2	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	Octahedral
	599.50	16680.57	10^4	LMCT	
	275.50	36297.64			
	245.00	40816.33			

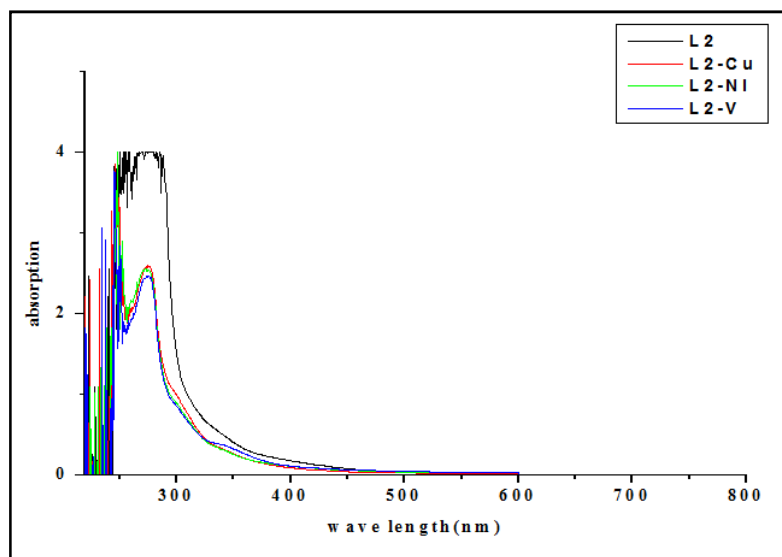


Figure 6. UV spectra for Ligand and its metal complexes

Table 3. FT-IR Spectral data for ligand and its metal complexes

Compounds	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{M}-\text{N})$ cm^{-1}	$\nu(\text{M}-\text{O})$ cm^{-1}	Free amine cm^{-1}
Ligand	1666.50	-	-	3363.86
Cu- complex	1620.21	692.44	480.28	-
Ni-complex	1651.07	613.36	470.63	-
V-complex	1606.70	547.78	466.77	-

The FT-IR spectrum of ligand confirms the formation of Imine bond ($-\text{C}=\text{N}-\text{H}$) and the absence of carbonyl bond ($\text{C}=\text{O}$). Actual band at $1643-1530\text{cm}^{-1}$ is assigned to stretching vibration of the imine group at ($-\text{C}=\text{N}-\text{H}$). The Schiff base showed the absence of bands at 1735cm^{-1} and 3420cm^{-1} due to carbonyl ($\text{C}=\text{O}$) and NH_2 Stretching vibration. A strong new band was observed at 1606.7cm^{-1} assigned to the azomethine ($\text{HC}=\text{N}$) linkage. It is suggested that amine and aldehyde moieties of the starting reagents are absent and have been converted into the azomethine moiety. The comparison of the IR spectra of the Schiff base and their metal chelates indicated that the functional group present in the metal complexes. Schiff base were principally coordinated to the metal atom in three ways, representing thus ligand acting in abidentate manner and the intermolecular H bonded OH group was around at 3446cm^{-1} . Ligand (L) was found to be 1666.50cm^{-1} . In all the complexes the co-ordination of the azomethine nitrogen to the metal centers. The $\nu(\text{M}-\text{N})$ bond was around at $466.67-480.28\text{cm}^{-1}$. The $\nu(\text{M}-\text{O})$ band was around at $547.78-678.94\text{cm}^{-1}$ the IR data shown in Table-3.

NMR – Spectra

NMR signal is usually plotted with magnetic field strength increasing to the right. Thus the signal for TMS appears at the extreme right of spectrum with $\delta=0\text{ppm}$. Greater the deshielding of protons, larger will be the value of δ . In L_1 NH_2 proton for the bidentate ligand appear at 7.74ppm and methoxy group at 3.83ppm and aromatic proton is multiplet in the range $6.22-8.21\text{ppm}$. In L_2 NH_2 proton for the bidentate ligand appear at 4.0ppm and aromatic proton appear at $6.6-7.4\text{ppm}$ and five membered ring appear at $6.3-7.4\text{ppm}$.

Anti-Microbial Studies

Antibacterial activity of compounds against bacterial pathogens using Well diffusion method

From the results it is inferred that metal complexes were more active than their ligands. The Copper (II) Schiff base complex show higher efficiency when compared with the standard.

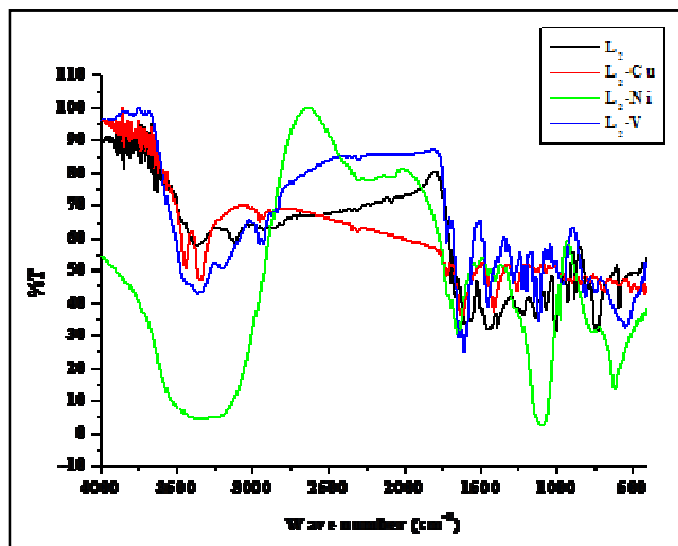
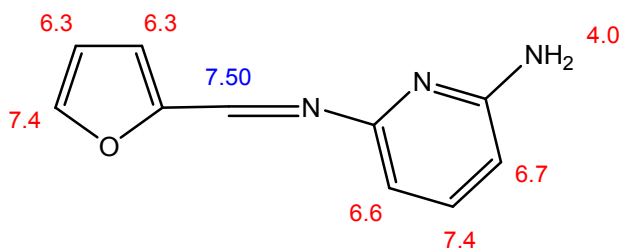


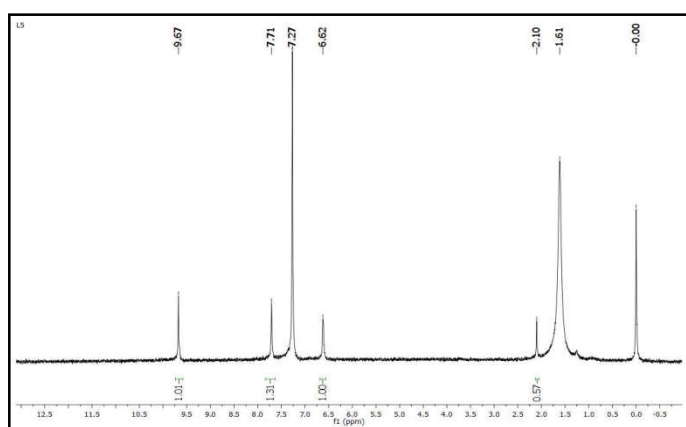
Figure 7. FT-IR spectra for Ligand and its metal complexes



$C_{10}H_9N_3O$
 Exact Mass: 187.07
 Mol. Wt.: 187.2
 m/e: 187.07 (100.0%), 188.08 (11.0%), 188.07 (1.1%)
 C, 64.16; H, 4.85; N, 22.45; O, 8.55

Figure 8. 2,6diamino pyridine-2-furaldimine
 1H -NMR- $CDCl_3$ -solvent; NH_2 -4.0ppm; ARH-6.6-7.4ppm
 FT-IR-KBr pellet; C=N -1666.50 cm^{-1} ; free amine-3363.86 cm^{-1}

This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane [29] and can be explained by Tweedy's chelation theory [30].

Figure 9. 1H -NMR spectrum for 2, 6 diamino pyridine-2-furaldimine

Antifungal activity of Ligand and its complexes against fungal pathogens using well diffusion method: From the results it is inferred that metal complexes were more active than their ligands.

The Nickel Schiff base complex show superior efficiency against *Aspergillusniger* and *Aspergillusflavus* fungi.

Table 4. Antibacterial activity of the Ligand and its complexes

Test Organisms	Zone of inhibition (in diameter)					Standard Amk 30 μg
	L	Cu	Ni	V	Solvent control	
<i>Staphylococcus aureus</i>	15	16	14	15	NZ	15
<i>Pseudomonas aeruginosa</i>	16	15	11	12	NZ	11
<i>Bacillus species</i>	13	17	13	14	NZ	12

Solvent used: DMSO (Dimethyl Sulphoxide) Standard used: Amikacin 30 μg

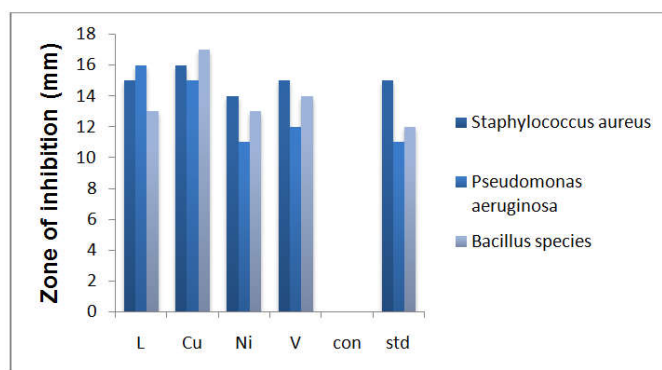


Figure 10. Antibacterial activity of the Ligand and its complexes

Table 5. Antifungal activity of the Ligand and its complexes

Test Organisms	Zone of inhibition (in diameter)					Standard Streptomycin
	L	Cu	Ni	V	Solvent control	
<i>Aspergillusniger</i>	16	18	19	16	NZ	15
<i>Aspergillusflavus</i>	15	15	17	14	NZ	13

Solvent used: DMSO (Dimethyl Sulphoxide) Standard used: Streptomycin

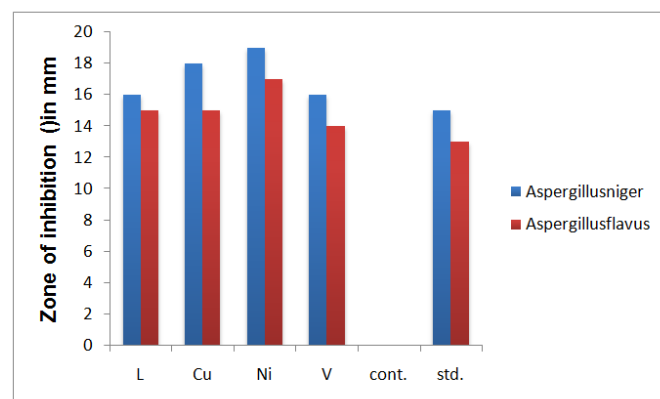


Figure 11. Antifungal activity of the Ligand and its complexes

Antioxidant Activity

DPPH Radical Scavenging Activity Assay: The scavenging activity of a chemical/or compound on the DPPH radical as a fast and reliable parameter to measure the *in vitro* antioxidant activity of such sample have been used by diverse researchers. This assay is based on the measurement of the decrease in molar absorptivity of DPPH at 517 nm after reaction with the test compound. The effect of antioxidants on DPPH radical scavenging is due to the hydrogen donating ability or radical scavenging activity of the samples. The scavenging reaction between (DPPH) and an antioxidant (H-D) can be written as:

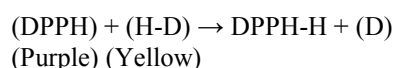
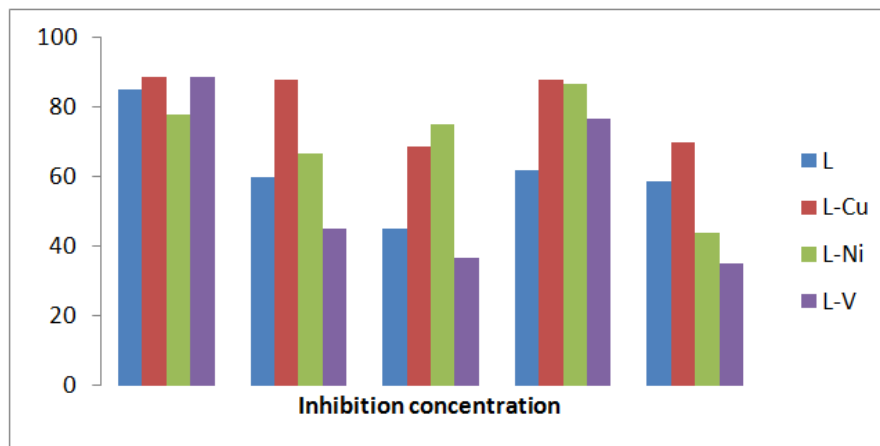


Table 6. Anti-oxidant activity for Ligand and its metal complexes

S.No	Complex	Concentration ($\mu\text{g/mL}$)				
		0.002	0.004	0.006	0.008	0.010
1.	L	85	60	45	62	59
2.	L-Cu	89	88	69	88	70
3.	L-Ni	78	67	75	87	44
4.	L-V	89	45	37	77	35

**Figure 12. Anti-oxidant activity for Ligand and its metal complexes**

Antioxidants react with DPPH, a stable free radical that is thus reduced, and as a result the absorbance decreases due to the formation of the DPPH-H from the DPPH radical. The degree of discoloration indicates the scavenging potential of the antioxidant compounds or samples in terms of hydrogen donating ability. It was observed that metal (II) complexes had higher activity than that of the free Schiff base. At the lowest concentration (100 $\mu\text{g/mL}$) the antioxidant activity of the free ligand was found to be 24.20% but, upon complexation, it increased significantly within the range 29.80%–45.01%.

Calculation: percentage of activity = $\frac{\text{blank} - \text{sample}}{\text{Blank}} \times 100$

Conclusion

Schiff base ligand derived from 2, 6-diamino pyridine with furaldehyde and its Copper (II), Nickel(II), and Vanadium(V) complexes have been synthesized. The ligand structure is confirmed by $^1\text{H-NMR}$ spectrum. The ligand and its complexes have been characterized by UV, FT-IR spectral techniques. Based on the spectral data the geometry of complexes can be predicted. Ni and V complexes are Octahedral and Cu complex has tetrahedral geometry. Anti-oxidant studies with different concentration of ligand and its metal complexes were also studied. The Scavenging activities at lower concentration will be greater. Copper(II) complex is having higher activity than other complexes. The Anti-microbial activities have also been studied. Copper complex has higher anti-bacterial activity and Nickel complex has higher Anti-fungal activity than the ligand. The complexes have highest anti-oxidant activity than the free ligand.

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