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Research Article

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Synthesis, Characterization and Biological properties of Schiff Base and Transition Metal Complexes

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ABSTRACT

In the present study an intermolecular reductive Schiff base formation from 2-nitro pyridine and 2-hydroxy benzaldehyde carried out in the presence of iron powder and ammonium chloride. The Schiff base transition metal complexes with Fe(II), Cu(II), Ru(III) and Rh(III) have been synthesized which were characterized by elemental analysis, molar conductance, magnetic susceptibility, electronic spectra, IR and ESR spectroscopy. The biological activities have also been studied for the synthesized compounds.

Keywords: Schiff Base metal complexes, molar conductance, IR spectroscopy, anti bacterial activities.

ARTICLE INFO

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1. Introduction

Schiff bases, as the most widely used organic compounds, have been widely used in synthesis of intermediates [1, 2], biological actions [3, 4], polymers [5, 6], and so forth and obtained a lot of progress. Schiff bases have been shown to exhibit a broad range of biological activities. Traditional formation of Schiff bases from nitroarene starting materials requires a two-step process in which the nitroarene is first reduced to the aniline, then isolated, and subsequently condensed with the desired carbonyl. Recently, catalytic Schiff base formation from nitroarenes and carbonyls has been reported. [7,8]

Green Context

In view of human health and environmental concerns, much attention is being paid to 'Green Chemistry', which is a chemical methodology to decrease or eliminate the use or generation of hazardous substances in the design, preparation and application of chemical production. Recent years have witnessed a major drive to increase the

2. Experimental

All the used chemicals and solvents were of AR grade and were used without further purification. All the reagents used for the preparation of Schiff base and metal salts were obtained from Loba chemie. The percentage compositions of the elements (CHNO) of the compounds were determined using an Elementar Vario Micro Superuser (CHNS) analyzer. The metal contents of the complexes were analyzed by ICPAES. The Infrared spectra were recorded as potassium bromide (KBr) discs using 8400S FTIR Perkin Elmer Spectrophotometer. The electronic Spectrum of complexes were recorded on ELICO SL -159 UV-Vis Spectrophotometer. The Electron spin resonance spectra (ESR) were recorded on Varian E-112 ESR Spectrometer. The molar conductivity measurements were made on ELICO CM - 180 model using methanol as the solvent. Magnetic susceptibility of complexes was measured by Gouy's method using mercury tetraisothiocyanatocobaltate as the callibrant.

Preparation of Schiff base ligand: 2-((pyridin-2-ylimino) methyl) phenol

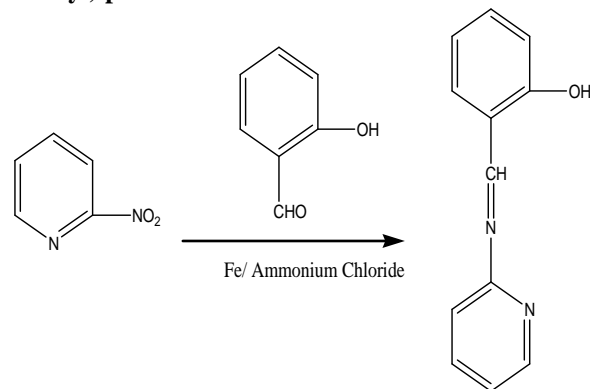


Figure 1

Ammonium Chloride (5.5 mmol) was added to a mixture of 2-nitro pyridine (1.0 mol), 2-hydroxy benzaldehyde (1.0 mmol), and iron powder (7.32 mmol) in 26 mL of EtOH–

efficiency of organic transformations while lowering the amount of waste materials. All the facts discussed above plus the increased interest in environmental protection issues inspired us to develop an efficient, mild and practical one pot synthesis of imines from aromatic nitro compounds. Tandem nitroarene reduction and intramolecular Schiff base condensation to give heteroarenes has been reported using iron in aqueous media. [9-11] surprisingly, the breadth of this methodology in an intermolecular application has not been previously reported. Korich developed a facile; an intermolecular reductive Schiff base formation from nitroarenes and benzaldehydes to yield diaryl imines is carried out in the presence of iron powder and dilute acid [12]. In this paper we describe the synthesis and characterization of Schiff base ligand prepared by condensation of 2-nitro pyridine and 2-hydroxy benzaldehyde and metal complexes with Fe(II), Cu(II), Ru(III) and Rh(III).

H₂O (2:1 v/v) solution. The reaction was heated to 90-100°C for 5-7 h before being filtered while hot. The filtrate was extracted using CH₂Cl₂ (3 × 25 mL) after which the organic layers were combined, dried over MgSO₄, filtered, and concentrated in vacuo to yield pale Yellow crystals dried in dessicator over phosphorous pentoxide yield 80%; melting point: 70-71°C.

Preparation of complexes with Schiff base ligand

The complexes of Fe(II) and Cu(II) were prepared by refluxing respective hydrated metal chloride in ethanolic solution of ligand in molar ratio of 1: 2 at pH 5 - 6. The resulting mixture was refluxed on water bath for 2 - 3 hrs. After cooling at room temperature, brown colored solid were separated out which was filtered, washed with water and then with ethanol. The resulting product was recrystallised and dried in vacuum desiccator over CaCl₂ anhydrous (yield 60 - 70%). For the preparation of Ru(III) and Rh(III) complexes, respective hydrated metal chloride were refluxed with ligand in molar ratio of 1:3 at pH 4 - 6 on water bath for 5 - 6 hrs. Brownish Black coloured product separate out on cooling which was collected by filtration, washed with water and then ethanol. The resulting product was recrystallised and dried in vacuum desiccator over CaCl₂ anhydrous (yield 40 - 50%). All the metal Complexes were found to be insoluble in water and soluble in most of common organic solvents.

Microbial studies

Antimicrobial activity of the synthesized Schiff base metal compounds was screened using the disc diffusion method against selected pathogens such as Escherichia coli. The compounds were dissolved in DMSO and sterilized by filtering through 0.45 μm millipore filter. Nutrient agar (anti bacterial activity) and sterilized by an autoclave (121° C and 15 lbs for 20 min) and transferred to previously sterilized petridishes (9 cm in diameter). Sterile whatmann filter paper discs (previously sterilized in U.V. lamp) were impregnated with synthesized compounds at a

concentration of 25,100 mg/disc was placed in the organism-impregnated petri plates under sterile condition. The plates were left for 30 min to allow the diffusion of compounds at room temperature. Antibiotic discs of Amoxycillin (100 µg /disc) used as positive control, while

DMSO used as negative control. Then the plates were incubated for 24 h at $37 \pm 1^\circ \text{C}$ for antibacterial activity. The zone of inhibition was calculated by measuring the minimum dimension of the zone of no microbial growth around the disc shown in figure 1

3. Results and Discussion

All the metal complexes are colored, solid, stable at room temperature and non-hygroscopic in nature. The Analytical and physical data of ligand and their metal complexes are

recorded in Table - 1. The metal complexes exhibit 1:2 and 1:3 (metal-ligand) stoichiometry.

Table 1

Compound	Mol Wt/melting point	Elemental analysis				eff B.M.	m $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
		Carbon	Hydrogen	Nitrogen	metal		
SB yellow	198.14 71° C	73.12 (72.73)	5.14 (5.05)	14.41 (14.14)	--	--	--
SB(Fe) ₂ Brown	450.13 300 C	64.01 (64.03)	3.90 (3.99)	12.40 (12.45)	12.40 (12.41)	5.13	38.70
SB(Cu) ₂ Brown	457.82 177° C	62.90 (62.96)	3.90 (3.93)	12.20 (12.24)	13.80 (13.89)	1.78	30.20
SB(Ru) hydrate Brownish black	710.52 60° C	60.80 (60.85)	3.75 (3.80)	11.80 (11.83)	14.20 (14.23)	1.81	24.10
SB(Rh)hydrate Brownish black	712.32 300 C	60.90 (60.97)	3.70 (3.79)	11.75 (11.80)	14.40 (14.45)	1.88	28.40

Infrared Spectral Analysis

Infrared spectra were recorded with a Perkin Elmer FTIR - 8400S Spectrometer (4000-400 cm^{-1}) using KBr pellets. On the basis of this, the presence of important functional groups in the compound can be identified. The Infrared spectrum of the ligand was compared with the spectra of Fe(II), Cu(II), Ru(III) and Rh(III) complexes. The typical IR spectra data was summarized in Table-2 along their assignment. The IR spectrum of the ligand shows broad band at 1610 cm^{-1} , which was assigned to due C=N stretching of azomethine group. In complexes this band was shifted to lower regions, 1604 cm^{-1} , 1605 cm^{-1} , 1607 cm^{-1} and 1608 cm^{-1} for Fe(II), Cu(II), Ru(III) and Rh(III) complexes respectively, suggesting the coordination of azomethine nitrogen to metal atom in complexation. This was due to the donation of electron density from Nitrogen to metal. IR spectrum of the ligand shows a weak band around 2750 - 3000 cm^{-1} due to intramolecular hydrogen bonded -OH group. This band is absent in the spectra of complexes indicating the dissociation of the phenolic

proton on complexation and involvement of phenolic anionic oxygen in coordination. Moreover, the strong band at 1280 - 1270 cm^{-1} due to C - O (phenolic) in the ligand has been shifted to the 1330 - 1319 cm^{-1} in the spectra of complexes. The strong absorption band due to pyridine ring occurring at 1495 cm^{-1} (C-N-C) has shifted to higher region by 25 - 40 cm^{-1} in the complexes showing the participation of nitrogen atom of pyridine ring in the complexation. The IR spectrum of Ru(III) and Rh(III) metal complexes exhibit a broad and strong absorption band in the region 3520 - 3170 cm^{-1} confirms the presence of (OH) absorption for lattice water. New bands were observed between 800 - 500 cm^{-1} region in the complexes, which were absent in the spectrum of ligand. The bands between 500-565 cm^{-1} were assigned to stretching frequencies of (M-O), the band between 471 - 450 cm^{-1} have been assigned to the stretching frequencies (M-N) respectively.

Table 2: IR spectra data along their assignment.

compound	(-OH)	(C=N)	(C-N)	(C-O)	(M-N)	(M-O)
SCB	2800	1610	1495	1277		
SCB(Fe) ₂	--	1604	1534	1328	535	450
SCB(Cu) ₂		1605	1531	1329	550	450
SCB(Ru) hydrate	3415	1606	1519	1319	561	471
SCB(Rh)hydrate	3438	1607	1519	1322	565	465

Molar Conductance

The molar conductance values of $1 \times 10^{-3} \text{M}$ solution of metal complexes in methanol were measured at room temperature (shown in Table - 1) using an ELICO International Journal of Chemistry and Pharmaceutical Sciences

Conductivity meter (cell constant 1.0 cm^{-1}). These values were compared with known molar conductivities which indicates the non - electrolytic nature of the complexes.

Electronic spectra and Magnetic susceptibility measurements of complexes

The electronic spectra were recorded on ELICO SL - 159 UV-Visible Spectrophotometer. The transition metal ions occur in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible spectroscopy. The electronic absorption spectra of Fe(II) complex exhibit the band around 18,867.92 cm⁻¹ (530nm) at room temperature which may be assigned to 5T_{2g} → 5E_g transition suggesting octahedral geometry and paramagnetic nature of complexes which is further supported by the magnetic moment value 5.15 B.M. The Cu(II) complex

Table 3: Electronic Spectra and Magnetic Moment of the Complexes

Metal complex	Band, max (nm)	assignments	eff (B.M.)
SCB(Fe) ₂	530	5T _{2g} , 5E _g	5.15
SCB(Cu) ₂	540	2E _g , 2T _{2g}	1.78
SCB(Ru) hydrate	550	2T _{2g} , 4T _{2g}	1.81
SCB(Rh)hydrate	510	2T _{2g} , 4T _{2g}	1.88

Electronic Spin Resonance Spectra

ESR spectra of complexes provide information about the extent of the delocalization of unpaired electron. In the present study, the ESR spectra of complexes have been recorded on X - band at frequency 9.5 GHZ under the magnetic field strength 3400 gauss in DMF at room temperature and their g , g , g_{avg} , g , and G values have been calculated. The values of ESR parameters for Fe(II), Cu(II), Ru(III) and Rh(III) complexes viz. g , g , g_{avg} , g , and G presented in Table - 4. ESR spectra of the complexes revealed two g values (g and g). the trend $g > g$ shows that the unpaired electron is delocalized in $d_{x^2-y^2}$ orbital in the ground state of metal and spectra are

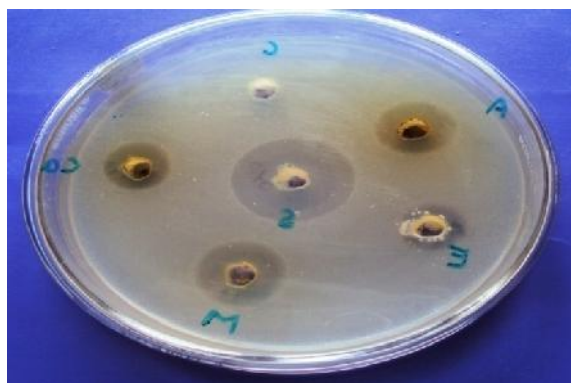


Figure 2: Description of markings on the petri plate. Observations after 24 hrs.

C - Control ca - Standard (amoxycillin) E – SCB Cu(II) 20 mg of the sample A–SCBFe(II) 20 mg of the sample S –

4. Conclusion

It can be concluded from the results of above study that Schiff base metal complexes acts as a very good tridentate

exhibit the band at 18,518.52 cm⁻¹ (540nm) which is assignable to 2E_g → 2T_{2g} transition suggesting octahedral geometry around Cu(II) ion. The Cu(II) complex showed magnetic moment value lie in the range 1.76 - 1.78 B.M. which is consistent with octahedral geometry. The Ru(III) and Rh(III) complexes display band at 18181.18 cm⁻¹ (550nm) and 19607.84 cm⁻¹ (510nm) which may be assigned to 2T_{2g} → 4T_{2g} transition suggesting octahedral geometry of complexes. The room temperature magnetic moment value of Ru(III) and Rh(III) complexes lie in the range of 1.73 - 1.90 B.M. attributed to Octahedral structure. Electronic Spectra and Magnetic Moment of the Complexes are listed in Table-3.

characteristics of axial symmetry. The parameter g_{avg} was obtained by equation $[(g_{avg}) = 1/3 (g + 2g)]$. Kvelson & Neiman²⁹ have reported that, $g > 2.3$ is the characteristics of an ionic environment and $g < 2.3$ indicates a covalent character in metal ligand bonding. Applying this criterion, in the present compounds g indicate the prevalence of covalent character in metal - ligand bond³⁰. The exchange coupling interaction has been explained by Hathaway expression $G = (g - 2) / (g - 2)$. According to Hathaway if the value of G is greater than four ($G > 4$), the exchange interaction is negligible whereas when the value of G is less than four ($G < 4$), a considerable exchange interaction is indicated in the complex. It is observed that G value for these complexes are less than four ($G < 4$), indicating considerable exchange interaction the complexes.

Table 4: Electronic spin resonance parameters of the complexes

Metal complex	g	g	g_{avg}	g	G
SCB(Fe) ₂	2.266	2.084	2.145	0.182	3.156
SCB(Cu) ₂	2.282	2.078	2.144	0.204	3.634
SCB(Ru) hydrate	2.250	2.076	2.135	0.173	3.226
SCB(Rh)hydrate	2.331	2.146	2.208	0.185	2.264

SCBRu 20 mg of the sample M – SCBRh 20 mg of the sample.

Proposed Structure of Complexes:

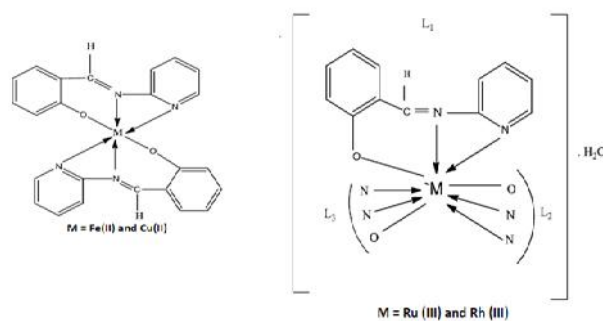


Figure 3

complexing agent towards many transition metal ions during complexation. All the metal complexes showed

enhanced microbiological activities as compared to ligand. The increase in the biological activity of metal chelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of

metal ion with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism.

5. Summary

The synthesized Schiff base metal compound showed more active than standard drug amoxicillin. The synthesized compound therefore, presents a new scaffold that can be

used to yield potent antimicrobial compounds. It can be concluded that these compound certainly holds great promise towards good active leads in medicinal chemistry.

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