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Preparation of Schiff base of 1, 2, 4-Triazole-4-amine with 3-Nitrobenzaldehyde, Its Complexation with Cu (II) and Zn (II) and Antimicrobial Activity of Complexes

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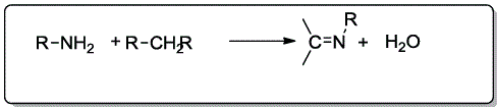
ABSTRACT

This study includes the synthesis of new derivatives of 1, 2, 4-triazole-4-amine derived from 3-nitrobenzaldehyde as a Schiff base. Co-ordination compounds of this Schiff base were synthesized and characterized by UV-Visible Spectroscopy, Infra-Red Spectroscopy, NMR, elemental analysis and magnetic measurement. These co-ordination compounds show biological activity against bacterial strains.

Keywords: 1, 2, 4- triazole-4-amine, Schiff base, Co-ordination compounds

INTRODUCTION

Schiff bases are the condensation products (following **Scheme 1**) [1] of primary amines and carbonyl compounds, named after Hugo Schiff, who discovered them in 1864 [2]. Schiff bases of aliphatic aldehydes are relatively unstable and are readily polymerized while those of aromatic aldehydes, having an effective conjugation system are more stable [3]. 1,2,4-triazole has been incorporated into a wide variety of therapeutically active drug [4,5] candidates including anti-inflammatory [6,7], antiviral, antimicrobial [8-11], analgesic [12], antitubercular [13-17] and anticancer properties [18-20]. People have synthesized some new 1, 2,4-triazole [21-24] and 1,3,4-triazole [25] derivatives with their antimicrobial activity [26,27].



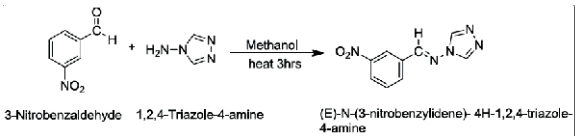
Scheme 1: General reaction of formation of Schiff base.

Schiff base ligands are potentially capable of forming stable complexes with metal ion [28-30]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications [31-33]. The biological properties of 1,2,4-triazole derivatives and their complexes impelled us to synthesize new Schiff base of 1,2,4-triazole-4-amine and its metal complexes. In the present investigation, we report synthesis, characterization of Schiff base derived from 1,2,4-triazole-4-amine and 3-nitrobenzaldehyde and its complexes with Cu (II) and Zn (II) and their antimicrobial activity.

MATERIALS AND METHODS

Preparation of ligand

3-Nitrobenzaldehyde (2.172 mmol) and 1,2,4-triazole-4-amine (2.38 mmol) were mixed in 5 ml methanol and the mixture was refluxed for 3 hrs on water bath. The white color product was obtained after the addition of 10 ml of ice water. The Schiff base was filtered and washed with ice water and dried at room temperature. It shows practical yield of 80% and M.P. is 238°C. Following reaction takes place (**Scheme 2**).



Scheme 2: Synthesis of Schiff base from 1,2,4-triazole-4-amine.

Characterization of ligand

The synthesized ligand was characterized by Spectrophotometer (Chemito UV-2100), Infra-Red Spectrophotometer (Bruker Optics, Model Alpha T), Bruker Advance II 400 NMR Spectrometer and elemental analysis by Perkin-Elmer 2400 CHN Analyzer. The physical parameters and result of elemental analysis were shown in **Table 1**.

Table 1: Characterization of ligand.

Sr. No.	Name and molecular formula of the ligand	Color	M.P.	% Yield	Elemental analysis Calculated (Found) %			
					C	H	N	O
1	(E)-N-(3-nitrobenzylidene)-4H-1,2,4-triazole-4-amine ($C_9H_7N_5O_2$)	White	238^{0}C	80	49.76 (49.74)	3.22 (3.20)	32.25 (32.22)	14.74 (14.70)

Synthesis of metal complexes

The solid complexes were prepared by mixing of aqueous solution of Copper chloride (0.264 mmol) and Zinc chloride (0.348 mmol) with 5 ml of 2% methanolic solution of ligand and refluxed for 2 hrs. Blue and white colored complexes were obtained for Copper (II) and Zinc (II) respectively (**Figure 1**).

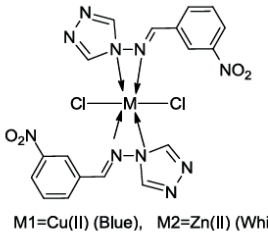


Figure 1: Proposed structure of metal ligand complexes.

Characterization of metal complexes

The metal complexes were characterized by UV Spectrophotometer (Chemito UV-2100), Infra-Red Spectrophotometer (Bruker Optics, Model Alpha T) and elemental analysis by Perkin-Elmer 2400 CHN Analyzer. The physical parameters and result of elemental analysis were shown in **Table 2**.

Table 2: Characterization of metal complexes.

Sr. No.	Name and molecular formula of the complex	Color	M.P.	% Yield	Elemental analysis Calculated (Found) %				
					C	H	N	O	M
1	Bis-(E)-N-(3-nitrobenzylidene)-4H-1,2,4-triazole-4-amino Copper (II) chloride $(C_9H_7N_5O_2)_2.CuCl_2$	Blue	318^{0}C	42.00	37.99 (37.96)	2.46 (2.43)	24.62 (24.60)	11.2 (11.20)	11.17 (11.15)
2	Bis-(E)-N-(3-nitrobenzylidene)-4H-1,2,4-triazole-4-amino Zinc (II) chloride $(C_9H_7N_5O_2)_2.ZnCl_2$	White	280^{0}C	21.12	37.86 (37.84)	2.45 (2.42)	24.45 (24.40)	11.22 (11.20)	11.46 (11.40)

Antimicrobial activity

The antimicrobial activity of the metal complexes was evaluated with the help of ATCC cultures including gram positive (*S. aureus*) and gram negative (*E. coli* and *P. aeruginosa*) using Gentamicin as standard and antifungal activity was tested against Candida sp. using Nystatin as standard and adopting standard protocols [34]. Saturated solutions of complexes in DMSO were used for the antimicrobial studies.

RESULTS AND DISCUSSION

The prepared complexes were found to be solids, insoluble in water but soluble in DMSO.

Electronic spectra

The characteristic peaks in electronic spectra of solutions of Schiff base in methanol and its complexes in DMSO are summarized in **Table 3**. The UV-Visible spectrum of Schiff base showed two bands at 319 and 327 nm (**Figure 2**). These two bands are observed due to π-π* transition. The UV-Visible spectrum of Cu (II) complex assigned to d-d transition. The spectrum of Cu (II) complex shows band at 332 nm which is attributed to the electronic transition of $2E_g \rightarrow 2T_{2g}$.

Table 3: Electronic spectra of free ligand and its complexes.

Product	λmax (nm)	Abs	Wavenumber cm^{-1}	Transition	BM
L	319, 327	2.158, 2.134	31347.96, 30581.03	π- π*,	-
CuL_2Cl_2	332	1.666	3010.48	π- π*, $^2E_g \rightarrow {}^2T_{2g}$	1.73
ZnL_2Cl_2	316	1.355	31645.56	π- π*	-

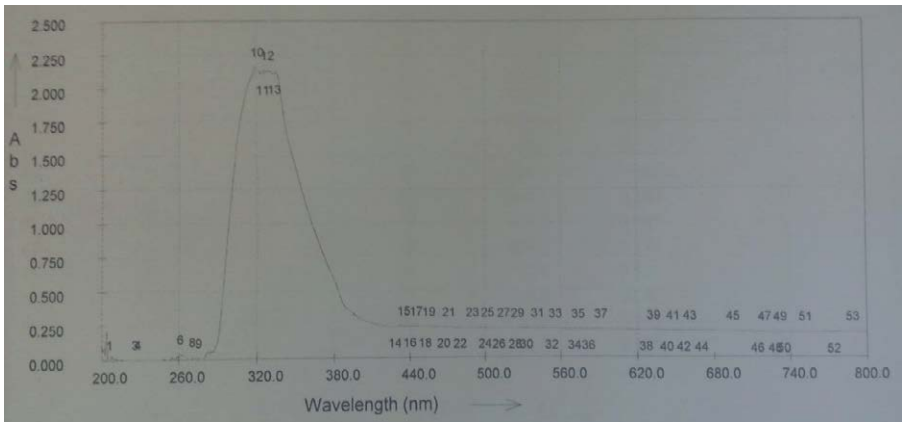


Figure 2: Electronic spectrum of Schiff base.

The electronic spectrum of Zn (II) complex were diamagnetic as expected for d^{10} ions, so that no d-d transition can be expected in the Zn (II) complex. The magnetic susceptibility measurements provide data to characterize the structure of complex. The magnetic moment for Cu (II) complex was approximately 1.73 BM. Zn (II) complex were diamagnetic and were no magnetic moment [35].

FTIR spectra

The structure of prepared ligand and complexes were confirmed by Infrared Spectroscopy. The characteristic bands in the IR spectra of ligand and complexes were reported in **Table 4**.

Table 4: IR spectra of free ligand and its complexes.

Product	Azomethine νC=N	Triazole νN-N	νM-N
L	1653.88	1285.32	-
CuL_2Cl_2	1645.45	1217.41	622.42
ZnL_2Cl_2	1629.87	1211.07	620.86

Nuclear Magnetic Resonance

The ^1H NMR spectra of ligand was recorded in DMSO. The ^1H NMR spectrum show sharp signals at δ 9.31 for one proton which could be attributed to the CH=N groups, aromatic proton in the δ 7.80-8.38 and two triazole proton shows a sharp signal at δ 8.71-9.07.

Antimicrobial activity

The synthesized metal complexes exhibited a biological activity against one gram positive, two gram negative and one fungus **Table 5**.

Table 5: Effect of complexes on antimicrobial bacteria.

Compound	*E. coli* ATCC 25922	*P. aeruginosa* ATCC 27853	*S. aureus* ATCC 25923	*Candida sp.*
CuL_2Cl_2	(-)	08 mm	08 mm	(-)
ZnL_2Cl_2	(-)	(-)	14 mm	(-)
Gentamicin(Standard)	22 mm	27 mm	31 mm	(-)
Nystatin (Standard)	(-)	(-)	(-)	22 mm
Note: (-) indicates no activity				

CONCLUSION

The complexes of Cu (II) and Zn (II) were synthesized by reaction of the synthesized ligand with the respective metal salts in 1:2 (M:L) ratio. The synthesized ligand and its complexes were characterized by UV-Visible, IR spectroscopic technique, NMR, magnetic susceptibility measurement, elemental analysis and their antimicrobial activity. The elemental and other spectral studies confirm the binding of Schiff base and metal ions and show the octahedral geometry of Cu (II) and Zn (II) complexes.

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