SYNTHESIS OF NEW SULPHANILAMIDE BASED SCHIFF BASE NICKEL COMPLEXES WITH STUDY OF ITS ANTIBACTERIAL ACTIVITY AND NANOPARTICLE SYNTHESIS

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ABSTRACT

Schiff base contains the Azomethine group prepared by reaction of the carbonyl group and amine group. In this project, Schiff bases of sulphanilamide on the treatment of imidazole-2-carboxaldehyde and Dehydroacetic acid have been synthesized. Further, their Nickel complexes have been synthesized. They were characterized by IR, Mass, NMR, UV-Vis spectra and found to have square planar geometry. They were screened with few bacteria and found to have good antibacterial activity against gram-negative bacteria. Further, NiO nanoparticles were synthesized by thermal decomposition of the above synthesized Nickel Schiff base complexes and found to have 93-98 nm particle size.

Keywords: Sulphanilamide, Schiff Base, Square Planar, Antibacterial Activity, Nanoparticles.

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INTRODUCTION

Schiff base simply contains Azomethine functional group and is synthesized by condensation of the carbonyl group with the amine.¹ This Schiff base has a unique property to bind with different metal ions increasing its applicability in the different fields. This Schiff bases have huge applications in most of the field especially in the pharmaceuticals as shown below in the Fig.-1 and even for the quantitative analysis, hence increasing attention of many researchers to derive more new Schiff base metal complexes.^{2,3}

Fig.-1: Applications of Schiff Bases

In the Present Study, we focus on the synthesis of Schiff base by combining sulphanilamide with two different aldehydes and study of its antimicrobial activity. It is an organic compound consists of an aniline derivative with the presence of sulphonamide group. Modern antibiotics have displaced sulphanilamide with some more efficient potent antibiotics. The Sulphanilamide based Schiff base metal complexes are of capable research interest owing to the prevalent antibacterial resistance in the pharmacy field. The

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stoichiometry of the formed Schiff base metal complex can be determined by slope ratio method, mole ratio method and jobs method of continuous variation.⁴

EXPERIMENTAL

Schiff base compounds were prepared by following the published standard procedures.⁵ all the chemicals were obtained from Merck.

Synthesis of Schiff Base I

(E)-4-(1H-imidazol-2-yl)methyleneamino)benzenesulfonamide

The above following Schiff bases are synthesized by reflux of mixture of aldehyde and aromatic amine in water. 1 millimole of each imidazole-2-carboxaldehyde and sulphanilamide in 10 cm³ distilled water was taken in the round bottom flask. This was refluxed for 3 hours. After completion of the reflux process, the content was cooled in air. The Schiff base was collected in solid-state, washed, recrystallized through ethanol and dried in a desiccator. The formed ligand is stable at room temperature. It is soluble in alcohol, chloroform at high temperature, DMSO and DMF.

Scheme-1: Synthesis of Schiff Base L₁

Synthesis of Metal Complex

The metal complex is produced by reflux of the ethanol solution of above-prepared ligand and Nickel chloride in 2:1 mole ratio, i.e. 2 millimoles of the above-prepared ligand in slight excess was taken in a round bottom flask with 25 ethanol. The Schiff base gets dissolved in it. 1 millimole of Nickel chloride was taken and dissolved in 5 cm³ of alcohol. This dissolved Nickel chloride was further added drop-wise in hot ligand solution. Few drops of dilute ammonia are added to maintaining its pH in the range of 7.5 to 8.0. The contents were refluxed for three hours. The precipitate of complex formed was filtered and washed with dilute ammonia and dried in a desiccator.

Synthesis of Schiff Base II

(E)-4-(1-(4-methyl-2,6-dioxocyclohex-3-enyl)ethylideneamino)benzenesulfonamide

Schiff base II is synthesized by reflux of mixture of DHA and sulphanilamide in alcohol. 1 millimole of both DHA and sulphanilamide was taken in 10 cm³ ethanol in the round bottom flask. It was refluxed for 3 hours. After refluxing, the content is cooled. The Schiff bases were collected in solid-state, washed, recrystallized through ethanol, and dried in a desiccator. This ligand is also stable at room temperature. It is soluble in alcohol, chloroform at high temperature, DMSO and DMF.

Scheme-2: Synthesis of Schiff Base L₂

Synthesis of Metal Complex

The metal complex is produced by reflux of the ethanol solution of above-prepared ligand and Nickel chloride in a 2:1 ratio, i.e. 2 millimoles of the above-prepared ligand in slight excess was taken in a round bottom flask with 10 ml ethanol. 1 millimole of Nickel chloride was taken and dissolved in 10 cm³ alcohol. This dissolved Nickel chloride solution was added drop-wise in hot ligand solution. Few drops of

dilute ammonia are added to maintain its pH in the range of 7.5 to 8.0. These were refluxed basically for 2 hours. The precipitate of complex formed was filtered and washed with dilute ammonia and desiccated.

RESULTS AND DISCUSSION

The Physical Properties of above Synthesised Schiff Bases are given in the following table and discussed in coming sections.

Table-1: Physical Properties of Schiff Bases

S. No.	Molecular Formula	Compound Code	Melting Point	Colour	Analytical Data				
					C	H	N	O	S
1.	C ₁₀ H ₁₃ N ₄ O ₂ S	L ₁	>300 ⁰ C	Yellow	48	5.2	22.4	12.8	12.8
2.	C ₁₅ H ₁₆ N ₂ O ₄ S	L ₂	>300 ⁰ C	Pale yellow	55.7	4.9	8.6	19.81	9.9

Spectral Analysis of Schiff Base L

Infra-Red Spectral Data

The data of IR spectra of the above synthesized Schiff base ligand shows –C=N– stretching band around 1800 cm⁻¹ and also one of the band at 1744.10 which can be consigned to the azomethine moiety, this confirms the condensation between the amino group of sulphanilamide and the ketone of DHA information of the Schiff base.^{6,7}

Fig.-2: IR Spectra of Schiff Base L₁

Mass Spectra

The Mass spectra revealed that molecular ion peak at m/e 249.12 indicates the formation of the Schiff base ligand which further undergoes fragmentations giving other smaller peaks.

Fig.-3: Mass Spectra of Schiff Base L₁

NMR Spectra

^1H NMR studies show the peak that δ 2.0 ppm of $-\text{NH}_2$ group attached to $-\text{SO}_2$ group. The peak from δ 6.71 to 7.71 multiplet is present for the Benzene ring. The peak at 3.3 ppm δ is for $-\text{N}=\text{CH}-$, methine group. 2.0 ppm δ for N-H group, 2.6 and 2.65 triplets for $>\text{CH}_2$ group of imidazole. The peak for one more $-\text{NH}_2$ group at around 3.5 ppm is not obtained indicating desired product formation.⁸

Spectral Studies of Schiff Base L_2

Infra-Red Spectral Data

IR spectra of the above synthesized Schiff base L_2 shows the IR band around 1685.69 cm^{-1} which can be assigned to the azomethine moiety, this confirms the condensation between the amino group of sulphanilamide and the ketone of DHA information of the Schiff base.

Fig.-4: IR Spectra of Schiff Base L_2

Mass Spectra

The Mass spectra revealed that molecular ion peak at m/e 323.3 indicates formation of the Schiff base ligand which further undergoes fragmentations giving other smaller peaks.

Fig.-5: Mass Spectra of Schiff Base L_2

NMR Spectra

^1H NMR studies show the peak that δ 0.9 ppm singlet and δ 1.71 ppm singlet of the methyl group of DHA. δ 2.0 ppm of $-\text{NH}_2$ group attached to $-\text{SO}_2$ group. 3.2 ppm δ singlet for the methane group. 3.17 and 3.02 ppm for the methylene group. Peak around 7.5 to 7.9 ppm multiplet indicates benzene. The peak for the para-substituted $-\text{NH}_2$ group is not found indicated undergoing condensation reaction.

Physical Properties of Above Synthesised Schiff Bases Metal Complexes

Table-2: Physical Properties of Schiff Bases Metal Complexes

S. No.	Molecular Formula	Compound Code	Colour	pH Range of Precipitation	M.P/ D.P. Temperature	Analytical Data (%)				
						C	H	N	O	Ni
1	NiC ₁₀ H ₁₃ N ₄ O ₂ S	Ni-L ₁	Green	7.5 -8.0	>300°C	43.01	4.6	20.06	11.4	10.4
2	NiC ₁₅ H ₁₆ N ₂ O ₄ S	Ni-L ₂	Dark Yellow	7.5 -8.0	>300°C	51.08	4.5	7.3	18.1	8.3

Conductivity and Electronic Absorption Data of Ni (II) Complexes

Table-3: Conductivity and Electronic Absorption Data of Ni (II) Complexes

S. No.	Compound Code	Molar Conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Magnetic Properties	Absorption Maxima cm^{-1} (nm)	
				${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ Weak	Charge Transfer Strong
1	Ni-L ₁	34.3	Diamagnetic	440nm(227000)	280nm(35714), 360nm (27700)
2	Ni-L ₂	29.2	Diamagnetic	560nm(17,857)	240 nm(41,666)

Fig.-6: Absorbance Vs. Wavelength Plot to obtain λ_{max} for Two Metal Complexes.

Octahedral Complexes generally consists of three bands in the range of 7000-13000 cm^{-1} , 10,000-20,000 cm^{-1} , 19,000 cm^{-1} - 27,000 cm^{-1} . Whereas, square planar complexes show strong absorption bands in the range of 15,000 to 25,000 cm^{-1} and 25,000-35,000 cm^{-1} and also very low absorption band near 11,000 to 13,000 cm^{-1} . Hence from the above data, it is revealed that complexes formed may have square planar structure.^{9,10}

Spectral Analysis of Metal Complexes

Infra-Red Spectral Data

IR spectra of the above synthesized Schiff base ligand L₁ displays IR band around 1700 cm^{-1} which is assigned to the $-\text{CH}=\text{N}-$ group get shifted to 1698.83 cm^{-1} , and band of 1744.10 cm^{-1} gets shifted to 1743.91 i.e. very marginally shifted towards lower side this confirms that azomethine donates its electrons to the Ni^{2+} forming metal complex. Also, a water molecule having broadband is observed around 3000 to 3500 cm^{-1} . The same nature of IR is plotted for other Schiff base-metal complex NiL₂.

Fig.-6: IR Spectra of Schiff Base Metal Complexes NiL₁ Fig.-7: IR Spectra of Schiff Base-Metal Complex NiL₂

IR spectra of the Schiff base L₂ shows IR band around 1685.69 cm⁻¹ which is assigned to the azomethine group get shifted to 1680.71 cm⁻¹, this confirms that azomethine donates its electrons to the Ni²⁺ forming metal complex. Hence, through all of the above data, we revealed that both the complexes have square planar geometry.

Antibacterial Properties

The Antimicrobial action was evaluated by the cup plate agar diffusion method by evaluating inhibition zones in millimeters.^{11, 12} In-vitro antimicrobial activity of the prepared Nickel Complexes and that of the standard have been estimated against four following bacteria strains which include gram-positive bacteria like *S. Aurious*, *S. Pyogen* and gram-negative bacteria like *E. Coli*, *P. Aeruginosa*.

The results of antimicrobial action of the complexes indicate that the complexes show good antibacterial activity against gram-negative bacteria whereas it didn't show activity against gram-positive bacteria.

Observations

Hence, the above-reported compound has very good antibacterial action against gram-negative bacteria whereas it doesn't have any action counter to gram-positive bacteria indicating is specific and selective in nature.

Scheme-3: Schiff base L_1 Metal Complex

Scheme-4: Schiff base L_2 Metal Complex

Table-4: Inhibition Values

Bacterium	ZONE Inhibition (mm)	
	Complex NiL_1 (1000 ppm)	Complex NiL_2 (1000 ppm)
<i>E.Coli</i>	14	15
<i>P.Aeruginosa</i>	14	16
<i>S.Aurios</i>	-----	-----
<i>S.Pyogen</i>	-----	-----

Nanoparticle Synthesis

Nickel oxide is also synthesized by the thermal decomposition method.¹³ The weighed quantity of above-synthesized Nickel-metal complexes was taken into silica crucible. The silica crucible was kept in a muffle furnace. The furnace was then heated at 700°C for 3 hours in a normal atmosphere. The product obtained after thermal decomposition was naturally cooled to room temperature. The residue obtained in silica crucible was used for further characterization.

Characterisation of SEM

SEM image indicates that obtained product NiO nanoparticles are highly crystalline. The microgram looks to be gentle and shows rough morphology. The appearance of particles is in an irregular spherical

shape. The particles are highly agglomerated and they are essentially clusters of nanoparticles. The observation of some larger nanoparticles may be due to its high surface energy and high surface tension. So we conclude that prepared NiO particles are in the Nano-meter range. The average diameter of the particles observed in 94 to 99 nm.

Nickel oxide is an important metal oxide with many uses, such as it is the vital foundation for several high-critical temperature superconductors and resources with giant magneto resistance, and is also used as pigments in dyes, catalysts in many organic reactions, semiconductor, solar cells, gas sensors, cathode materials and magnetic loading media.¹⁴

Fig.-1: Cup Plate Method Determining Activity against *P. Aeruginosa*

Fig.-2: Cup Plate Method Determining Activity Against *E. Coli*.

CONCLUSION

The composition of these Metal ligand complexes can be confirmed by the Slope ratio method, mole ratio method and jobs method of continuous variation^{15, 16}. All the results as mentioned above with the help of IR, Mass, NMR, UV-Vis spectra also reveals that the two prepared Nickel complexes have proposed 1:2 metal to ligand stoichiometry with square planar geometry. The estimated antimicrobial activity suggests that the complexes are having good antibacterial activity against gram-negative bacteria and hence may assist as means of transportation for initiation of the ligand as standard cytotoxic compounds. Also, the synthesized NiO Nanoparticles have good size in the range of 95 nm which can have a wide variety of applications and its further study needs to be revealed as it has application in the field of semiconductor, solar cells, storage media and pharmacy and cathode materials.

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