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Synthesis, Characterization and Antimicrobial Activities of Schiff Base Derived from Acetylacetone and 2-aminopyridine and its Cobalt(II) and Nickel(II) Complexes

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ABSTRACT

Metal(II) complexes and its Schiff base derived from acetyl acetone and 2-aminopyridine have been synthesized and investigated by different physicochemical techniques. The complexes were synthesized by refluxing the methanolic solution of the Schiff base and Co(II) and Ni(II) chlorides which results in the formation of the Co(II) and Ni(II) complexes in good yield. The Schiff base and metal(II) complexes were characterized by using FTIR, solubility test, decomposition temperature, molar conductance, UV-visible spectrophotometry (Job's method), and gravimetric analysis. The Schiff base and their cobalt(II) and nickel(II) complexes were tested for antimicrobial activities against some pathogenic bacteria and fungi: *Staphylococcus aureus, Streptococcus pyogens, and Salmonella typhi, Aspergillus formigatus, Rhizopus spp. and Mucor spp.* respectively, using paper disc diffusion method. The melting point of the Schiff base were 115-120 ^{0}C of m.pt while decomposition temperature of the Co(II) and Ni(II) complexes obtained at the range of 198 and 207 $^\circ$C respectively. The Schiff base is insoluble in H_2O, CCl_4, but slightly soluble in methanol, ethanol, acetone, nitrobenzene, and petroleum ether and completely soluble in dimethylsulphoxide and dimethylformamide. The cobalt(II) and nickel(II) metals complexes were soluble in DMSO and DMF and insoluble in water, carbon tetrachloride, and nitrobenzene and petroleum ether. The IR spectral data revealed azomethine peak of the Schiff base at 1600 cm^{-1} while for the cobalt(II) and nickel(II) metals complexes, the peak was found within 1611 cm^{-1}– 1605 cm^{-1}supporting coordination of Schiff base/ligands to respective Co(II) and Ni(II) metals. Magnetic moment values of the synthesized cobalt(II) and nickel(II) complexes obtained were in the range of 4.30 –3.38 BM which suggested the complexes are paramagnetic. Molar conductance values were within the range of 5.2–6.05 $\Omega^{-1}cm^2mol^{-1}$ which

revealed that all the complexes are non-electrolytic in nature. .The metal Schiff base complexes exhibited higher antimicrobial activity than the free Schiff base.

Keywords: Acetyl Acetone, 2-Aminopyridine Schiff base, metal(II) complexes, characterization and Antimicrobial activity

INTRODUCTION

Schiff bases is a chemical compound containing carbon and nitrogen double bond (-HC=N-) [1, 2]. It is derived on the addition of an amine to a compound containing a carbonyl functional group, aldehyde or ketone, to produce an imine, which is also known as azomethine. The oxygen atom in the carbonyl group (>C=O) is replaced by a nitrogen atom to give an imine group (>C=NR where R≠ H). A Schiff base acts as a ligand because it usually contains –N and –O donor atoms [3]. Schiff bases of both natural and non-natural origin, have exhibited varied range of applications including antibacterial, antitubercular, antifungal, antiparasitic, antiviral, antioxidant, anticancer, analgesic, catalytic and anti-inflammatory properties [1, 2, 4]. Transition metal Schiff base complexes play very vital roles as they are known to possess biological activities such as anticonvulsant, antibacterial, antiviral and antidiabetic [5]. Schiff base complexes could be used as corrosion inhibitors as well as antifungal and antifouling agents [6]. Schiff bases derived from acetylacetone and p-methoxyaniline showed great activity against some bacteria like *Staphylococus aureus, Bacillus sutilis, Escheriachia coli* and fungi, *Aspergillus niger* [6]. The paper provide a new insight into the influence of chemical structure of imin/azomethine compounds on their physico chemical properties and potential anti-microbial application.

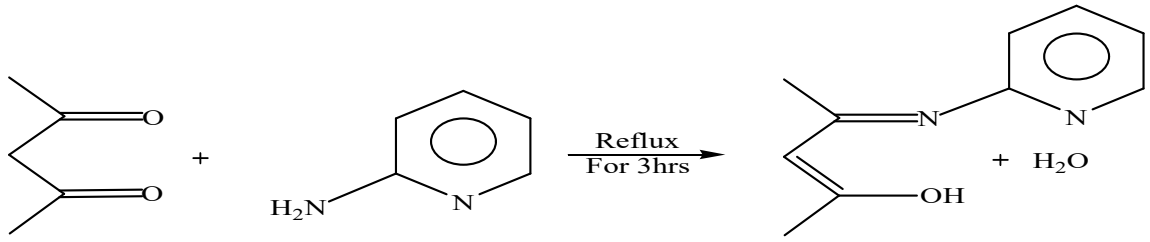
The advantage of preparation of schiff's base lingands and their complexes is the activity of antimicrobial. This investigation indicates whether the final product is active microbial. So the anti-microbial activities of the ligands as well as the complexes are necessary for study.

MATERIALS AND METHODS

Reagents of analytical grade were used without further purification. All glasses as used were well washed with detergent, rinsed with distilled water and dried in an oven at 110 °C. All weightings were carried out on an electric Metler balance model B154, melting point and decomposition temperature were determined using gallenkamp melting point apparatus. Molar conductivity was determined using Jen way 4010 model. FT-IR spectral analysis was recorded on a Fourier Transformed spectrophotometer 8400S model.

Preparation of Schiff base

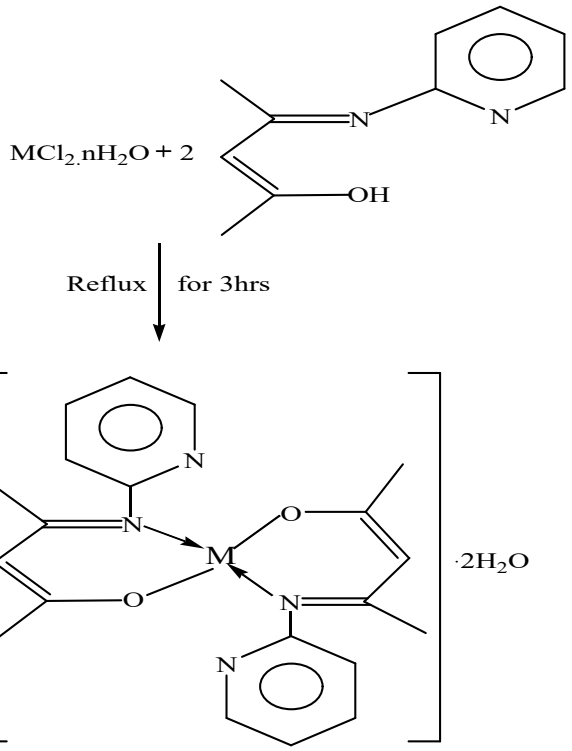
Equimolar methanolic solution of 2-aminopyridine (0.941 g, 0.01 mol) was mixed with acetyl acetone (1.027cm^3·0.01 mol). The resulting mixture was refluxed for 3 hours and the solid product formed after cooling in ice was filtered, purified by recrystallization from methanol and finally dried in desiccator over P_2O_5 for 18 hours [1].



Scheme 1.

Preparation of Metal(II) Complexes

The metal complexes were synthesized by mixing methanolic solution (50 cm^3) of the Schiff base (0.01 mol) with a methanolic solution (50 cm^3) of the manganese chloride (0.01 mol). The resulting mixtures were refluxed for three hours. On cooling, complex that precipitated out was filtered, washed with methanol and ether and dried over P_2O_5 for 18 hours in desiccators [4].



Scheme 2

Antibacterial Activity

The *in vitro* antibacterial activity of the Schiff base and its Metal(II) complexes was assayed by agar disc diffusion method using cultures of *Staphyllococcus aureus, Staphylococcus pyogen* and *Salmonella typhi.* The Schiff base and its complexes were separately dissolved in DMSO to have concentration of 60, 30 and 15 µg/cm^3 respectively. Amoxicillin was used as reference drug, while DMSO wetted dics was used as a negative control.

Antifungal Activity

The *invitro* antifungal activity of the Schiff base and its corresponding metal(II) complexes was assayed by agar dics diffusion method using cultures of *Aspergillus formigatus, Rhizopus Spp.* and *Mucor Spp.* Using various concentration of 60, 30 and 15 µg/cm^3 respectively. Ketoconazole was used as reference drug, while DMSO wetted dics was used as a negative control.

RESULTS AND DISCUSSION

Results of several analyses of the synthesis acetyl acetone and 2-aminopyridine and its Metal(II) complexes are in Tables 1-9.

Table 1: Physical Properties of the Schiff base and its Metals(II) Complexes

Compounds	Formular Weight(g/mol)	Colour	Percentage Yield	Melting Point (˚C)	Decomposition Temperature (˚C)
Ligand	176	Brown	75.90	120	–
$[CoL_2].2H_2O$	447	Pale blue	81.82	–	198
$[NiL_2].2H_2O$	446	Light green	78.25	–	207

Ligand = $C_{10}H_{12}N_2O$

Table 2: Solubility test of the Schiff base and its Metals(II) Complexes

Compounds	H_2O	CH_3OH	C_2H_5OH	CCl_4	C_3H_6O	$C_6H_5NO_2$	C_6H_{14}	DMF	DMSO
Ligand	IS	SS	SS	IS	SS	SS	SS	S	S
$[CoL_2].2H_2O$	IS	SS	SS	IS	SS	IS	IS	S	S
$[NiL_2].2H_2O$	IS	SS	SS	IS	SS	IS	IS	S	S

Ligand (L) = $C_{10}H_{12}N_2O$ S = Soluble, IS = Insoluble, SS = Slightly Soluble, DMF=Dimethylformamide, DMSO =dimethylsulphoxide

Table 3: Molar Conductance of the Metals(II) Complexesin DMSO Solution

Compounds	Concentration $(moldm^{-3}) \times 10^{-3}$	Specific Conductance $(ohm^{-1}cm^{-1}) \times 10^{-6}$	Molar Conductance $(ohm^{-1}cm^{-1}mol)$
$[CoL_2].2H_2O$	1.00	5.20	5.20
$[NiL_2].2H_2O$	1.00	6.05	6.05

Table 4: Infrared spectral data of the Schiff base and its Metals(II) Complexes

Complexes	$\nu(C=N)cm^{-1}$	$\nu(M–N)cm^{-1}$	$\nu(MO)cm^{-1}$	$\nu(OH)cm^{-1}$
Ligand	1600	–	–	3332
$[CoL_2].2H_2O$	1611	724	491	3319
$[NiL_2].2H_2O$	1605	720	454	3362

L= Ligand

Table 5: Magnetic Susceptibility Value of the Co(II) and Ni(II) Metals Complexes

Compounds	Gram magnetic susceptibility (X_g) (g^{-1})	Molar Magnetic Susceptibility (X_g) (mol^{-1})	μeff (B.M)
$[CoL_2].2H_2O$	3.907×10^{-5}	7.935×10^{-3}	4.30
$[NiL_2].2H_2O$	6.68×10^{-6}	3.36×10^{-5}	3.38

L= ligand

Table 6: Average percentage composition by weight of metal ion in the Complexes

Complex	Weight of ppt. (g)	Average weight of metal in the complexes = G.F× W.ppt (g)	Percentage composition of metal in the complex
			Calculated
$[CoL_2].2H_2O$	0.1320	0.023364	11.68
$[CuL_2].2H_2O$	0.1397	0.0285	14.25

L= ligand, G.F = Gravimetric factor, Wppt = Weight of precipitate

Table 7: Determination of water of crystallization in the Complexes

Complexes	Initial mass (g)	Final mass (g)	Loss in mass	% of water
$[CoL_2].2H_2O$	0.2	0.187	0.013	6.5
$[NiL_2].2H_2O$	0.2	0.185	0.015	7.5

L= ligand

Table 8: Sensitivity Test of the Schiff base and its Co(II) and Ni(II) Metals Complexes against selected Fungal Isolates

Test organism	Compound	Zone of inhibition conc. (µg/disc)		
		60	30	15
Aspergillusformigatus	Ligand(L)	12	13	10
	$[CoL_2].2H_2O$	16	15	10
	$[NiL_2].2H_2O$	14	12	08
	Standard	32	26	15
*Rhizopus*spp.	Ligand (L)	10	10	08
	$[CoL_2].2H_2O$	16	14	06
	$[NiL_2].2H_2O$	15	10	06
	Standard	31	19	14
*Mucor*spp.	Ligand (L)	12	10	06
	$[CoL_2].2H_2O$	14	06	06
	$[NiL_2].2H_2O$	14	08	06
	Standard	32	18	12

Standard = Ketoconozole(200mg)

Table 9: Sensitivity Test of Schiff base and its Co(II) and Ni(II) Complexes against some Bacterial Isolates

Test organism	Compound	Zone of inhibition conc. (µg/disc)		
		60	30	15
Staphylococcus aureus	Ligand (L)	16	15	12
	$[CoL_2].2H_2O$	16	14	10
	$[NiL_2].2H_2O$	17	16	14
	Standard	27	19	18
Staphylococcus pyogens	Ligand (L)	17	14	12
	$[CoL_2].2H_2O$	20	16	15
	$[NiL_2].2H_2O$	20	16	14
	Standard	30	23	18

Salmonella typhi	Ligand (L)	16	15	08
	$[CoL_2].2H_2O$	15	13	06
	$[NiL_2].2H_2O$	18	14	13
	Standard	25	23	21

Standard = Amoxicillin (500 mg)

Figures 1-5 are the FTIR spectra.

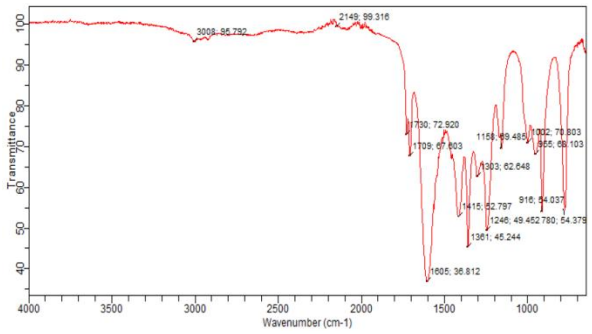


Fig. 1: cetyl acetone (ACAC)

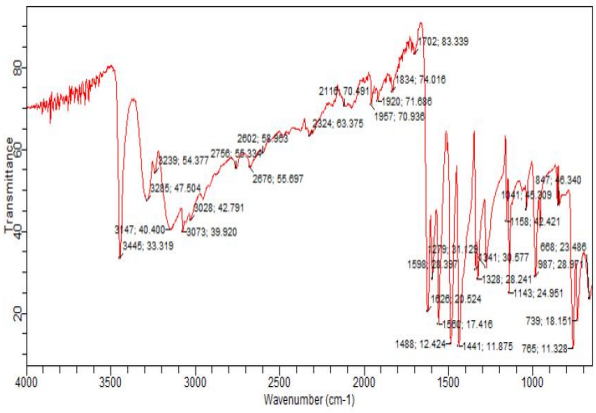


Fig 2: 2-amino pyridine

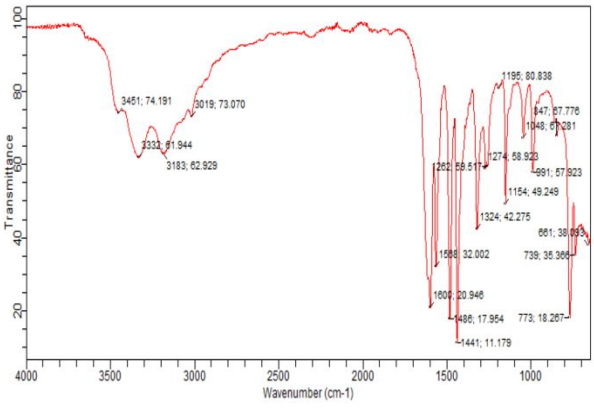


Fig 3: Schiff base

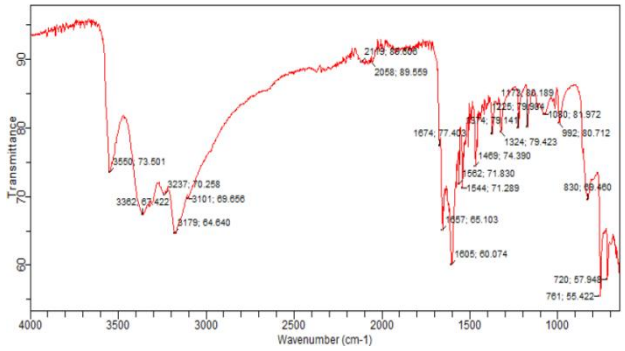


Fig 4: Co(II) Complex

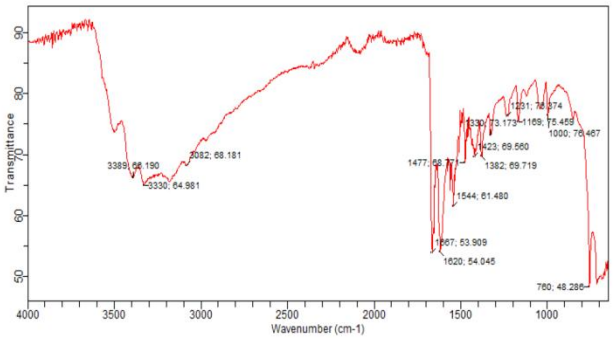


Fig 5: Ni(II) complex

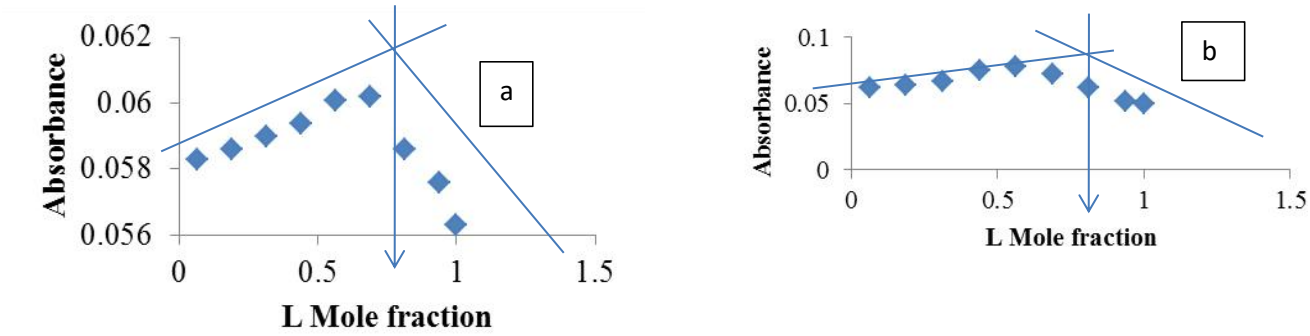


Fig 6a: Plot of absorbance against ligand mole fraction at λ_{max}620nm for Co(II) complex

Fig 6b: Plot of absorbance against ligand mole fraction at λ_{max}700nm for Ni(II) complex

The Schiff base was synthesized by condensing equimolar solution of acetyl acetone and 2-aminco pyridine (Scheme 1). The Schiff base was obtained as light brown crystals with a melting point of 120 $^{\circ}$C and percentage yields of 75%. Complexation of Schiff base and corresponding Metal(II) salts produced stable complexes of Co(II) and Ni(II) obtained to be pale blue and light green colours with percentage yields of 81.82% and 78.25% for Co(II) and Ni(II) complexes respectively.

The complexes decomposed at a temperature range of 198 - 207 $^{\circ}$C, thus confirming stability as affirmed by the work of Osowole *et al.* [2]. The high decomposition temperature suggested a good thermal stability of the complex as shown in Table 1.

The solubility test of the Schiff base and its metal(II) complex were soluble in dimethyl isulphoxide (DMSO), and dimethyl formamide (DMF). This may be attributed to their high polarity but insoluble in carbon tetrachloride (CCl_4), nitrobenzene and petroleum ether as shown in Table 2.

Metal-ligand ratio was determined using Job's method of continuous variation (UV-visible) [3]. This is an agreement with report of Tomasevich *et al.*[4].

The molar conductance values (Table 3) of the synthesized complex obtained was in the range of 5.20 – 6.05 $ohm^{-1}mol^{-1}cm^{-3}$.. These low values suggested that the complexes are non electrolytes. Similar results were reported in the literature [5, 6].

The magnetic moment of the complex determined at room temperature were in the range of 4.30 – 3.38 BM. This positive value indicated that the complex is paramagnetic. The

percentage composition of the metal ions, were found gravimetrically. The result obtained was in good agreement with calculated values as seen in Table 6. The same procedure was adopted by Yoder [7] in determining similar metal ions.

The percentage of water of crystallization in the complexes was determined and the results in Table 7 confirmed the presence of water of crystallization in the complex with 8.0% [8]. The percentage composition of the ligand was determined by difference and the results obtained were within the calculated value.

The empirical formulae of the metal(II) complex was determined from the percentage compositions of the metal(II) ion, the ligand and the water of crystallization. The results obtained suggested the general formula, $[MnL_2]2H_2O$.

The FT-IR spectra were recorded in KBr pellet using Agilent Technology FT-IR spectrometer (4000–400) cm^{-1}. The significant IR band for the ligand as well as its complexes are compiled and presented in Table 4 in the IR spectrum of the Schiff base ligand a sharp band observed at 1600cm^{-1} is assigned to the ν(–C=N–H) mode of azomethine group. This band is shifted to the of 1605 cm^{-1} in the spectra of the complex indicating coordination of the azomethine nitrogen atom to the central metal ion and is supported by the appearance of new peaks in the range of 763 cm^{-1} in the spectra which was due to metal to nitrogen bond (M – N) [9]. A band at the range of 3293 cm^{-1} is due to ν(C–OH) phenolic group was observed in the ligand which is formed as a result of tautomerism. The disappearance of phenolic ν(OH) band in the complex suggested that coordination by phenolic oxygen after deprotonation with metal ion. This is further supported by shifting of ν(C–O) phenolic band to higher frequency in all the complexes. The appearance of band at the range of 491 cm^{-1} is due to ν(M–O) suggested by deprotonation of OH of the ligand. In the IR spectra of the complexes there is bands at the range of 3362 cm^{-1} is observed suggesting water crystallization in the complexes [10] (Table 7). This indicated the presence of water crystallization in the complexes.

The ligand and its synthesized metal(II) complex was screened for antibacterial and antifungal activities against three bacterial isolates (*Staphylococcus aureus*, *Streptococcus pyogens* and salmonella typhi) and three fungal isolates (*Aspergillus fungitus,Rhizopus* spp. and *Mucor* spp) using disc diffusion method in DMSO respectively. The Schiff base and its metal(II) complex showed good activity against all the tested organisms. However the activity is more at higher concentration in al cases. Comparative studies show that the Metal (II) complex show

significant activity than the ligand but lower than the reference drugs as can be seen in Tables 8 and 9. The result obtained are similar to that of Prakash and Adakhari [12].

CONCLUSION

The Schiff base ligand derived from condensation of 2-aminopyridine with acetyl acetone and its Metal(II) complexes has been synthesized and characterized by solubility test, melting point, decomposition temperature, molar conductance, magnetic susceptibility, FTIR analysis, UV visible, and gravimetric analysis. The antimicrobial activity of the ligand as well as the Metal(II) complex were tested. The FTIR anslysis revealed that the ligand is bidentate. Molar conductance of the complexes show low values which demonstrated the nonelectrolytic nature of the complexes. The melting point and decomposition temperature of the ligand and complex showed good thermal stability. The UV-visible confirmed that the metal: ligand ratio is 1:2, and the gravimetric method of analysis confirmed the empirical formula of the complexes as $[M(C_{10}H_{12}N_2O)_2]2H_2O$. The magnetic susceptibility measurement values of the complexes revealed that all the complexes are paramagnetic. The results of the antimicrobial tests revealed that the biological activity of the ligand is enhanced when presented in the form of a metal (II) complexes

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