Synthesis, Characterization and Antibacterial Analysis of Some Schiff Base Metal (II) complexes

Comment [u1]: Rephrae to IUPAC Name Synthesis, Characterization and Antibacterial Activity of some of its Metal (II) Complexes

Abstract

The complexes of Co (II), Mn (II) and Ni (II) with the Schiff base (IUPAC name) synthesized from acetyl acetone and 2-aminobenzoic acid were characterized by molar conductance, magnetic susceptibility, Infrared and elemental analyses. The solubility test on the Schiff base and its metal (II) complexes revealed their solubility in most organic solvent except chloroform and diethyl ether. The molar conductance of the complexes was high indicating that they are strong electrolytes. The antibacterial susceptibility test conducted on the Schiff base and the metal (II) complexes showed a good activity except Ni (II) complex.

Comment [u2]: Conductivity should be used and abstract corrected to reflect topic

Introduction

A coordination compound consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agent [1].The name coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. In coordination compounds the donors are usually the ligands, and the acceptors are the metals. Coordinate covalent bonds formally formed by combining one electron from each atom; only the formal electron counting distinguishes them [2].

Schiff bases are condensation products of primary amines with carbonyl compounds. They were first reported by Schiff in 1864, [3]. The common structural feature of these compounds is the azomethine group with the general formula RHC=NR', where R' and R is alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted [4]. As a result of the relative simple preparation, synthetic flexibility, and the special property of azomethine group (C=N), Schiff bases are generally excellent chelating agents [4] especially when a functional group like -OH or –SH is present close to the azomethine group so as to form five or six membered ring with a metal ion. Versatility of Schiff base ligands and biological, analytical, and industrial applications of their complexes make further investigations in this area highly desirable [4]. Thus, the research focused on the synthesis, characterization and exploring antimicrobial activity of the Schiff base and the complexes of cobalt (II), nickel (II), and manganese (II).

Materials and Method

Materials

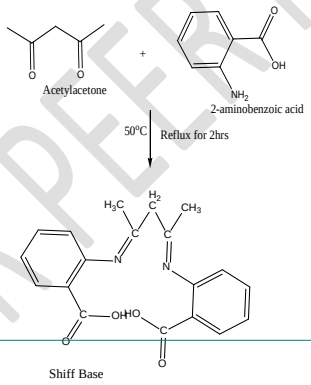
All chemical reagents, 2-Aminobenzoic acid, acetylacetone, and solvents were of analytical grade and were obtained from LOBA Chemie, Park Scientific Ltd, UK and JHD and used

without any purification. The microorganisms (clinical isolates) used for the antimicrobial analysis were obtained from Microbiology Department, Usmanu Danfodiyo University, Sokoto.

Synthesis of the Schiff base IUPAC NAME and the metal complexes

The Schiff base was prepared by adding 25 cm^3 of x M acetyl acetone ethanolic solution (1.0269 cm^3, 0.01 mol) to the same volume of ethanolic solution of (y M) 2-amino benzoic acid (2.7428 g, 0.02 mol). The resultant mixture was refluxed for two hours at about 50 °C. The solution was concentrated on steam bath and then allowed to cool in an ice bath. The dark brown product that precipitated was recrystallized from hot ethanol. The crystals were then filtered and dried in a desiccator over phosphorous pentaoxide [5].

The cobalt complex was prepared by adding 25 cm^3 of ethanolic solution of x M cobalt chloride (2.3393 g, 0.01 mol) with ethanolic solutions of the prepared Schiff base (3.3864 g, 0.01 mole). The resulting mixture was refluxed for two hours after which the solution was concentrated on a steam bath and cooled in ice cold water. The precipitate was filtered and washed repeatedly with hot ethanol until the washing was colourless. The obtained product was dried in a desiccator over phosphorus pentoxide [5,6]. The same procedure was adopted for the synthesis of manganese and nickel complexes.



Scheme 1: Synthesis of the Schiff Base

Comment [u3]: Rephrase to. 'The Schiff base (IUPAC name) was synthesized by addition of 25 CM^3 of n M acetyl acetone ethanolic solution to the same volume of y M 2-amino benzoic acid ethanolic solution'.

Comment [u4]: Rephrase to show concentration of reacting species from calculated reacting mole ratios

Comment [u5]: Name Schiff base

Characterization of the Schiff base IUPAC NAME and the complexes

Fourier-transform infrared spectroscopy (FTIR) and elemental analyses

The FTIR spectra of the Schiff base and complexes were recorded in the range of 4000 - 650cm^{-1} using Cary 630 FTIR spectrometer at the Department of Chemistry, Bayero University, Kano. The percentage mass of carbon, hydrogen, nitrogen and oxygen were determined by using PerkinElmer CHNS/O elemental analyser at the Universiti Tecknologi Petronas (UTP), Malaysia.

Determination of melting point, molar conductivity, magnetic susceptibility and solubility test

The melting points of the ligands (only one ligand was used) and the complexes are uncorrected as determined by Gallenkemp melting point apparatus. For the molar conductivity, a solution of each metal (II) complex (0.02 g/ml) was prepared in dimethyl sulfoxide and the molar conductance was measured using the Jenway conductivity meter. The molar conductance of the complexes was obtained using the relation:

Molar Conductance = $\frac{1000K}{C}$ where K = specific conductance, C = molar concentration.

The magnetic Susceptibility of the complexes is determined by placing an empty capillary tube inside the magnetic susceptibility balance, and the value recorded as R_o. Small quantity of the complex is then placed in to the capillary tube and, the value R and length L of the sample in the tube are also recorded respectively. The magnetic susceptibility (Xg) was obtained using the relation:

$$Xg = \frac{CL(R-R_o)}{10^9M}$$

Where M is the mass of complex in the capillary tube (W_1-W_o) and C is the proportionality constant which is always = 1.

The solubility of the Schiff base and the metal complexes were carried out in distilled water, methanol, dimethyl sulfoxide, hexane, ethanol, acetone, and diethyl ether. A 10 mg of each of the metal complex was dissolved in 2 cm^3 of corresponding solvent to determine their solubility [7].

Antibacterial studies of the Schiff base IUPAC NAME and metal (II) complexes

The *in vitro* antibacterial were tested against two pathogenic bacteria: *Streptococcus pyogenes* (gram positive) *and Pseudomonas Auriginesa* (gram negative). They were collected from the microbiology research laboratory, Usman Danfodiyo University, Sokoto. The bacteria were sub cultured on nutrient agar media and incubated at 37 °C for 24 hrs. Three concentrations (50, 100, and 150 mg/mL) of both the Schiff base and the complexes were made using DMSO solvent. Ditch Well diffusion method was used to assay the antibacterial.

Comment [u6]: hours

Preparation of media for antibacterial test

A 2.8 g of nutrient agar was weighed and dissolved in 100 mL distilled water in a conical flask which was then heated on a hot plate to dissolve the powder completely followed by autoclaving at 121 °C for 15 mins. It was then allowed to cool and was poured in to petri dishes to solidify.

Comment [u7]: Use minutes

Preparation of MacFarland turbidity standard solution

The turbidity standard was prepared by mixing 99.5 cm^3 of 1% v/v sulphuric acid and 0.5 cm^3 of 5 mMole barium chloride ($BaCl_2.2H_2O$). The solution was mixed thoroughly and dispense in test tubes [8].

Antibacterial assay

The antibacterial effect of the complexes and the Schiff base was performed using the procedure described by [9]. A sterile Muller Hinton agar was prepared and poured into the petri dishes and allowed to solidify. A loop full of each organism was stricken on the surface of the solidified media and each plate properly labeled. Wells are made in each plate using a sterile cork borer (6 mm), after which the concentration of each extract was dispensed into the bored holes alongside the antibiotic (streptomycin) which serve as the control. The plates were left to stand to allow diffusion of the extract after which it was incubated at 37 °C for 24 hrs. The diameter of zone of inhibition were measured and recorded using a meter rule. These activities were performed three times and reported as mean of all the three readings.

Results and Discussion

The results of the various analyses carried out are presented below. The interaction between acetyl acetone and 2-aminobenzoic acid gives a shiny brown Schiff base of 68% yield with a melting point of 213 °C, indicating good stability. The melting point might be associated with the strong attractive forces due to intermolecular hydrogen bond. The reaction mixture of the Schiff base and the metal chloride of Mn (II), Co (II), and Ni (II) in ethanol yielded 61.53 - 73.13% of the metal (II) complexes. They were isolated as crystals stable in atmospheric condition and are pale brown, brown, and green colours, with a melting point ranging between 97 to 165 °C as shown in Table 1 [10].

Comment [u8]: Give IUPAC name

Table 1: Some physical properties of the ligand and the complexes.

Complexes	Color	Yield (%)	Molecular weight	Melting point (°C)
HL^1	Brown	68.0	338.36	213
$[Mn(HL^1)].4H_2O$	Pale Brown	61.53	465.32	165

Comment [u9]: Already gotten

$[Co(HL^1)].2H_2O$	Green	88.57	433.33	97
$[Ni(HL^1)].4H_2O$	Pale Brown	73.13	469.07	107

The band at 1615 cm^{-1} in the Schiff base spectral data was as assigned to stretching vibration mode of *v*(C=N). The spectral of the metal (II) complexes assignable to *v*(C=N) vibration mode, undergoes a shift to lower wave number in the range of 1588 - 1598 cm^{-1} on coordination. The band within 409 - 431 cm^{-1} and 455 – 480 cm^{-1} are attributed to *v*(M-N) and *v*(M-O) stretching vibrations respectively, confirming coordination of the Schiff base to the respective metal ions (Table 2). The bands in the region 3371 - 3473 cm^{-1} was attributed to *v*(O-H) stretching frequency for water of crystallization in the metal (II) complexes [11,12]. The elemental analyses (C, N, and H) of the Schiff base and the complexes were determined and presented in Table 3. The result obtained is in good agreement with the 1:1 metal to Schiff base ligand ratio.

Table 2: Infrared spectral data of the ligand and the complexes.

Compounds	*v* (C=N)	*v*(C=C)	*v*(O-H) (cm^{-1})	*v*(M-N)	*v*(M-O)
HL^1					
$[Mn(HL^1)].4H_2O$	1588	1460	3371	480	431
$[Co(HL^1)].2H_2O$	1592	1469	3393	455	422
$[Ni(HL^1)].4H_2O$	1598	1467	3473	474	409

Table 3: Elemental results of the complexes and the ligands (%).

	Calculated(found)		
Complexes	**C**	**H**	**N**
Schiff Base	67.45(67.40)	5.36(5.40)	8.28(8.22)
$[MnL].4H_2O$	49.04(49.1)	5.63(5.70)	6.02(6.08)
$[CoL].2H_2O$	52.67(52.60)	5.12(5.20)	6.46(6.50)
$[NiL].4H_2O$	48.65(48.69)	5.59(5.62)	5.97(6.03)

Table 4 showed magnetic susceptibility values for the metal (II) complexes in the range of $6.1x10^{-6}$ to $2.5x10^{-5}$g. They are all positive values, suggesting that the complexes are paramagnetic in nature. The molar conductance values of the metal (II) Schiff base complexes in DSMO solution were determined in the range of 752 - 1460 $ohm^{-1}cm^2mol^{-1}$ (Table 5). This is a very high value, suggesting that the metal (II) Schiff base complexes are strong electrolyte [13].

Table 4: Magnetic properties of the metal (II) complexes

Complex	R_o	R	L (cm)	M (W - W_o) g	Xg (cm)
$[MnL].4H_2O$	-037	946	1.9	0.075	$2.5x10^{-5}$
$[CoL].2H_2O$	-038	183	2.0	0.086	$1.6x10^{-5}$
$[NiL].4H_2O$	-037	720	1.8	0.073	$6.1x10^{-6}$

Table 5: Conductivity measurement of the metal (II) complex in DMSO

Complexes	Concentration (mg/L)	Specific conductivity ($ohm^{-1}cm^2$)	Molar conductivity ($ohm^{-1}cm^2mol^{-1}$)
$[Mn(HL^1)].4H_2O$	$2x10^{-2}$	292.0	1460
$[Co(HL^1)].2H_2O$	$2x10^{-2}$	271.6	1358
$[Ni(HL^1)].4H_2O]$	$2x10^{-2}$	150.4	752

The solubility test of the Schiff base and its metal (II) complexes were carried out in various solvent. The Schiff base is soluble in acetone, methanol, DMSO, ethanol, and hexane, slightly soluble in diethyl ether but insoluble in water and chloroform. The metal (II) complexes are soluble in acetone, DMSO, ethanol and hexane but slightly soluble in chloroform and diethyl ether. Mn (II) and Co (II) complexes were slightly soluble in distilled water, chloroform and diethyl ether, whereas Ni (II) complex is insoluble in water but slightly soluble in diethyl ether as shown in Table 6.

Table 6: Solubility test of the Schiff base and the complexes

Solvent	Ligand	[MnL].4H_2O	[CoL].2H_2O	[NiL].4H_2O
Water	NS	SS	SS	NS
Acetone	S	S	S	S
Methanol	S	S	SS	S
Chloroform	NS	SS	SS	SS
DMSO	S	S	S	S
Ethanol	S	S	S	S
Hexane	S	S	S	S
Diethylether	SS	SS	SS	SS

S = Soluble, NS =Not Soluble, SS=Slightly Soluble.

The antibacterial test carried out showed a good activity on the ligand and two of the complexes of Co (II) and Mn (II)] (Figures 1 and 2). However, the Ni (II) complex did not show any activity on the bacteria used.

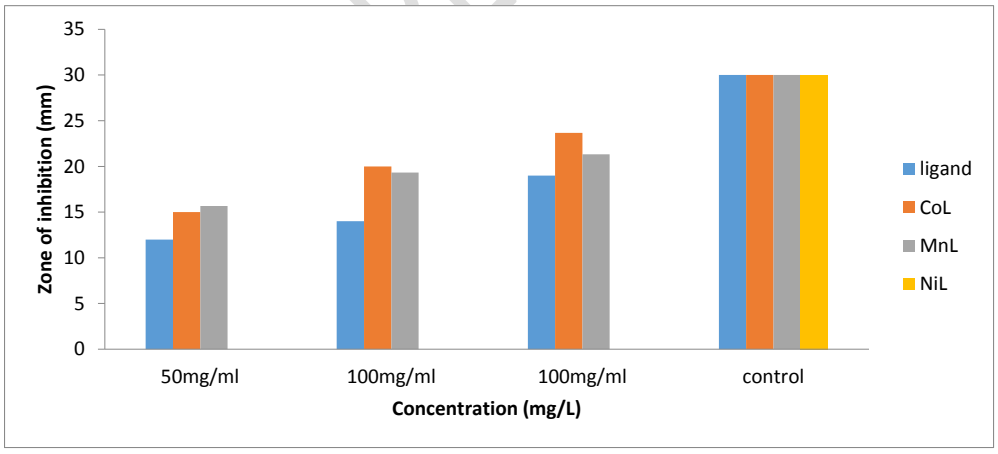


Fig. 1: Antibacterial activities of the Schiff base and complexes against clinical isolate *Streptococcus Pyogens*.

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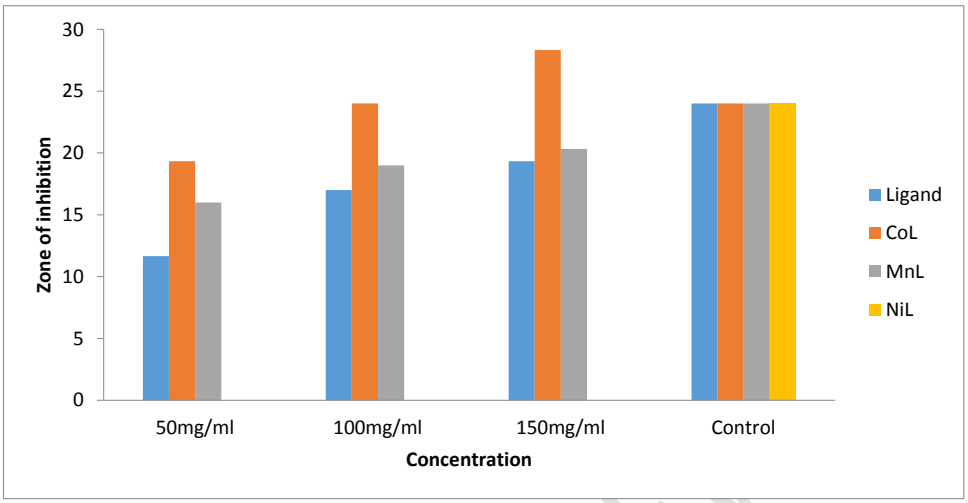

Fig. 2: Antibacterial activities of the Schiff base and complexes against clinical isolate *Pseudomonas auriginasa*.

Comment [u12]: Control should have a different legend as against one showing it is a combination of Schiff base and all metal complexes and charts should indicate standard deviations since three replicate experiments were done and values are reported as mean.

Conclusion

The Schiff base was prepared by the condensation of 2-aminobenzoic acid and acetyl acetone. The metal (II) complexes were also prepared by the reaction of ethanolic solution of the Schiff base and the ethanolic solution of the metal (II) chloride. The complexes were isolated as solid powders, stable in atmospheric conditions and are of different colours, high percentage yield, and are characterized by high melting points/decomposition temperature. The conductivity measurement of the complexes showed a very high value revealing that they are very good electrolytes. The solubility test was carried out in different solvents such as water, acetone, ethanol, and DMSO etc. The coordination in the complexes occurs through the N atom of the amine and also through the deprotonated O atom of the OH group from -COOH. IR spectral data of the Schiff base confirm the existence of C=N group, suggesting the formation of the Schiff base. The elemental analyses of the complexes are in good agreement with those of the proposed structure. The Schiff base IUPAC name and its manganese (II) and Cobalt (II) complexes displayed a good antibacterial activity against all the tested microorganisms at 50 mg/ml, 100mg/ml, and 150 mg/ml.

References

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