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Synthesis, characterization and antimicrobial studies on Schiff base derived from 4-amino-2-hydroxybenzoic acid and 2-hyroxybenzaldehyde and its cobalt (II) and nickel (II) complexes

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ABSTRACT
A Schiff base derived from the reaction of 4-amino-2-hydroxybenzoic acid with 2-hydroxybenzaldehyde and its metal (II) complexes of Co (II) and Ni (II) were synthesized. The IR spectral data revealed that the coordination was through the azomethine nitrogen and phenolic oxygen indicating that the Schiff base is bidentate. The molar conductance of the Co and Ni complexes were found to be 25.9 and 15.8 Ω-1cm2 Mol-1 respectively which indicated that, the complexes were non - electrolytes. The decomposition temperature of Ni (II) and Co (II) complexes were found to be 285 and 290 oC respectively, showed that the complexes are stable. The Ni (II) and Co (II) complexes exhibit Magnetic moment values of 1.79 and 5.63 BM, which suggested the complexes, are paramagnetic. Determination of metal: ligand ratio was done using Job's method of continuous variations. The result showed a metal:ligand ratio 1:2. The biological screening of the Schiff base and its metal (II) complexes were studied against three bacterial and two fungal isolates; Staphylococcus aureus, Escherichia coli and Pseudomonas aeruginosa, Mucor indicus and Aspergillus flavus. Septrin and Nystatin were used as control for the bacteria and fungi respectively. The result revealed that the complexes exhibit higher activities than the Schiff base but lower than the control.

KEYWORDS
4-amino-2-hydroxybenzoic acid; 2-hydroxybenzaldehyde; Schiff's base; Characterization; Antimicrobial activity

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INTRODUCTION
A Schiff base is type of chemical compound containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group. These compounds were named after Hugo Schiff in 1864 when he reported the condensation of primary amine with carbonyl compounds. The common structural feature of these compounds is the azomethine group with a general formula of RHC = NRI, where; R and RI are alkyl, aryl, cycloalkyl or heterocyclic group which may be variously substituted [1].

A Schiff base is able to coordinate metal ions through the imine nitrogen and another group, usually linked to an aldehyde. Schiff bases are able to stabilize many different metals in various oxidation states by controlling the performance of metals in a large variety of useful catalytic transformations. Most Schiff bases have NO or N2O2-donor groups but the oxygen atoms can be replaced by Sulphur, nitrogen, or selenium atoms, which make them good chelating agents, and they be can easily be prepared and characterized [2].

[3] reported the preparation of the Mn (II) and Ni (II) complexes with the Schiff base derived from the salicylaldehyde and 2-aminobenzoic acid. The complexes were characterized by gravimetric, molar conductance and infrared spectral analysis. The Schiff base and its Ni (II) complex were found to be soluble in most organic solvents, except ether, acetonitrile and tetra chloromethane. The molar conductance of the complexes measured were low, indicating their non- electrolytic nature.

[4] reported on synthesis, characterization and antimicrobial studies of salicylic acid complexes of some transition metals (II) Co (II), Mn (II) and Zn (II). The preliminary investigation of antimicrobial activities of the metal complexes revealed that the inhibitory ability of the metal complexes is notably higher than the ligand, though less than the control.

MATERIALS AND METHODS

All the reagents used in this work were of analytical grade and used without further purification. All glass wares used were washed with detergent, rinsed with distilled water and dried in the oven at 110^{o}C before used. The weighing was carried out on electrical Metler balance Toledo B154. The infrared (IR) spectra were recorded using Fourier Transformed Infrared Spectroscopy (FTIR CARY 630 Agilent technologist). The melting point and decomposition temperature were determined using Gallekemp melting point apparatus. Magnetic susceptibility was determined using Sharwood MK1 balance. The molar conductance measurement was carried out using Jenway 4010 model conductivity meter. The antimicrobial screening was conducted by disc diffusion method at Department of Microbiology, Bayero University Kano.

• Preparation of the Schiff Base

4-aminosalicyclic acid (1.531g, 0.01 mol) and 2-hydoxybenzylaldehyde (1.22g, 0.01mol) solution in 50 cm^3 methanol was refluxed for two hours. The reaction mixture was cooled for 24 hours, a yellow precipitate was obtained which was filtered, washed with cold ethanol and dried in a desiccator over $CaCl_2$ for a week [5].

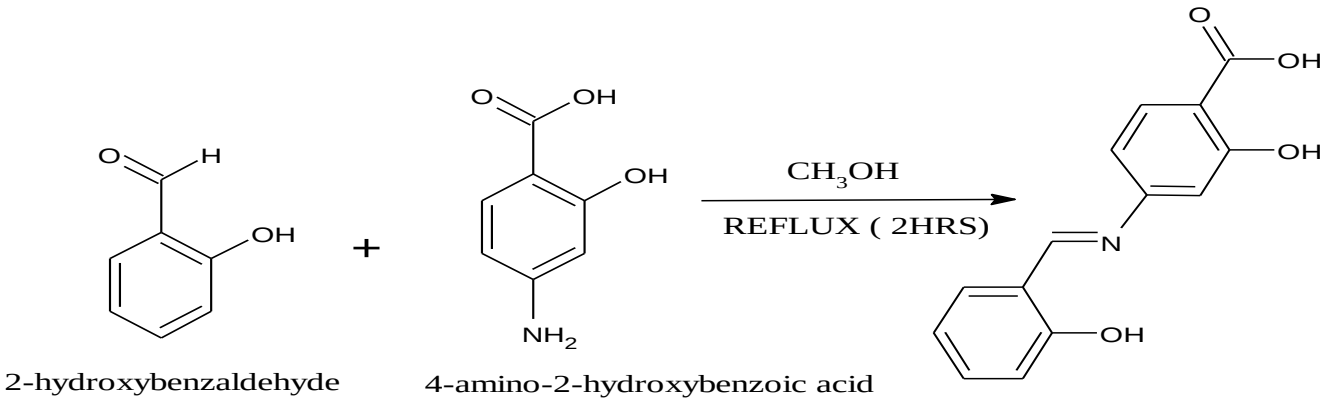

FIGURE 1: Reaction pathway for preparation of Schiff base

• Preparation of the Metal (II) Complexes

Schiff base (5.14g, 0.02 mol) and nickel (II) chloride (2.376g, 0.01mol) was dissolved in 50 cm3 of methanol and then refluxed for 2 hours. The precipitate formed was filtered off, washed with ethanol and petroleum ether and dried in a desiccator over anhydrous calcium chloride for one week. The same procedure was adopted for the cobalt (II) complex [4].

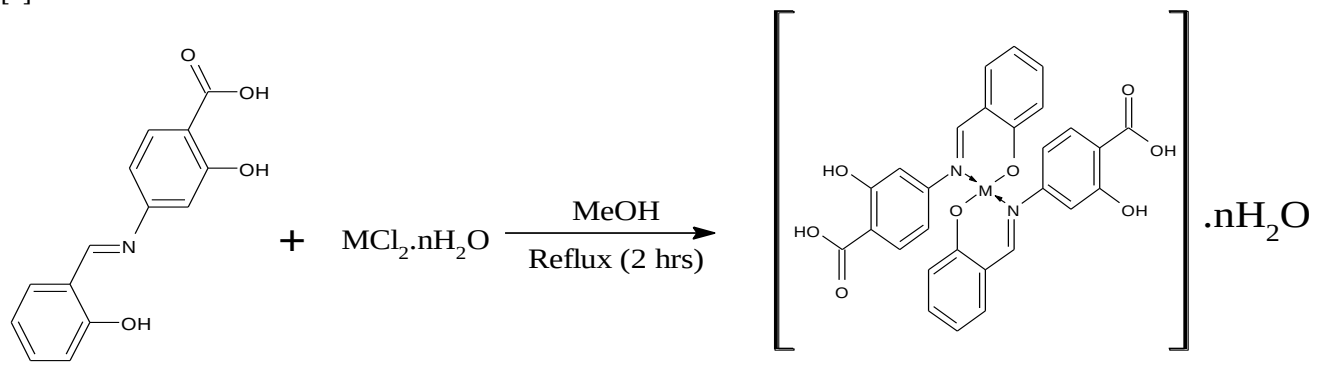

FIGURE 2: Reaction pathway for preparation of metal (II) complexes

• **Antibacterial and Antifungal Activities Test**

The Schiff base and complexes were screened for their activity against clinically isolated bacteria and fungi. The Schiff base and the complexes were dissolved separately in DMSO to produced three different concentrations (15µg, 30 µg, and 60 µg) per disc. The prepared disc of the ligand and complexes together with standard antibiotic disc were placed on to the surface of the incubated media at an interval and incubated at 37^{o}C for 24 hours. The diameter of the zone of inhibition produced by the ligand and the complexes were measured and compared with the standard antibiotics while DMSO wetted dics was used as negative control [6].

RESULTS

The results of the characterization, antibacterial and antifungal activities of the Schiff base and its metal (II) complexes are presented in the tables below.

TABLE 1: Physical Properties of the Ligand and its Metal (II) Complexes

Compound	Colour	Melting point (^{o}C)	Decomposition Temperature (^{o}C)	Percentage yield (%)
L	Yellow	185	-	76.3
$[CoL_2].2H_2O$	Pale brown		285	88.6
$[NiL_2].2H_2O$	Light green		290	76.9

L = $C_{14}H_{11}NO_4$

TABLE 2: Solubility Test of the Ligand and its Metal (II) Complexes

Compound	Water	MeOH	Ethanol	Acetone	Chloroform	Benzene	DMSO	DMF
L	IS	S	IS	IS	SS	SS	S	S
$[CoL_2].2H_2O$	IS	SS	IS	S	SS	IS	S	S
$[NiL_2].2H_2O$	IS	SS	SS	SS	IS	IS	S	S

L = $C_{14}H_{11}NO_4$

Where ; S = Soluble, SS = Slightly Soluble, IS = Insoluble

TABLE 3: Conductivity Measurement of Complexes in (1 x 10^{-3}) DMSO Solution

Complexes	Concentration (Mol dm^{-3})	Specific conductance (Ohm^{-1} cm^{-1})	Molar conductance ($Ohm^{-1}cm^{-2}mol^{-1}$)
$[CoL_2].2H_2O$	1 x 10^{-3}	25.9 x 10^{-6}	25.9
$[NiL_2].2H_2O$	1 x 10^{-3}	15.8 x 10^{-6}	15.8

L = $C_{14}H_{11}NO_4$

TABLE 4: Magnetic Susceptibility Value of the Metal (II) Complexes

Complexes	Magnetics Susceptibility (cm^{-3} g^{-1})	Molar Magnetics Susceptibility (cm^{-3} mol^{-1})	B.M (µeff)
$[CoL_2].2H_2O$	1.5909x10^{-5}	9.751x10^{-3}	4.82
$[NiL_2].2H_2O$	6.4535 x 10^{-6}	3.953 x 10^{-3}	3.33

L = $C_{14}H_{11}NO_4$

TABLE 5: Infrared Spectral Data of the Ligand its Metal (II) Complexes

Compounds	V(C=N) cm^{-1}	V(M-N) cm^{-1}	V(M-O) cm^{-1}
L	1574	-	-
$[CoL_2].2H_2O$	1587	598	438
$[NiL_2].2H_2O$	1566	611	476

L = $C_{14}H_{11}NO_4$

TABLE 6: Percentage Composition by Weight of Metal in the Complexes

Complexes	Percentage Composition of the Metals in the Complexes.	
	Calculated	Observed
$[CoL_2].2H_2O$	10.31	9.71
$[NiL_2].2H_2O$	10.28	10.46

L = $C_{14}H_{11}NO_4$

Table 7: Job's Methods of Continuous Variation Results of the Metal (II) Complexes

S/N	Ni (II) Complexes (λ_{max} = 420nm)		Co (II) Complexes (λ_{max} = 681nm)	
	X_L	Abs	X_L	Abs
1	0.083	0.1032	0.083	0.0820
2	0.167	0.1213	0.167	0.0864
3	0.250	0.1222	0.250	0.0871
4	0.333	0.1195	0.333	0.0966
5	0.417	0.1395	0.417	0.0981
6	0.500	0.1323	0.500	0.1001
7	0.583	0.1576	0.583	0.0110
8	0.667	0.1624	0.667	0.1172
9	0.750	0.1469	0.750	0.1068
10	0.833	0.1449	0.833	0.1046
11	0.917	0.1078	0.917	0.0105
12	1.000	0.0989	1.000	0.1020

X_L = Mole Fraction; Abs = Absorbance

TABLE 8: Determination of Water of Crystallization in the Complexes

Complex	Initial Mass (g)	Final Mass (g)	Loss Mass (g)	% of Water
$[CoL_2].2H_2O$	0.2001	0.1844	0.0157	7.85
$[NiL_2].2H_2O$	0.2000	0.1854	0.0146	7.30

$L = C_{14}H_{11}NO_4$

TABLE 9: Determination of Empirical Formulae of the Complexes

Sample	Ni (II)	L	H_2O	Co (II)	L	H_2O
% by Mass	10.28	82.42	7.30	10.31	81.84	7.85
Moles	0.1752	0.3207	0.4056	0.1750	0.3184	0.4361
Mole ratio	1	2	2	1	2	2
Empirical Formula	$[NiL_2].2H_2O$			$[CoL_2].3H_2O$		

$L = C_{14}H_{11}NO_4$

TABLE 10: Results of Antibacterial Activities of the Schiff Base and Its Metal (II) Complexes

Test Organisms	*Staphylococcus aureus*			*Escherichia coli*			*Pseudomonas aeruginosa*		
Concentration (µg/disc)	**60**	**30**	**15**	**60**	**30**	**15**	**60**	**30**	**15**
Ligand	6	6	6	6	6	6	9	6	6
$[CoL_2].2H_2O$	15	13	10	15	13	12	15	13	11
$[NiL_2].2H_2O$	11	8	7	7	6	6	6	6	6
Septrin	27	27	27	38	38	38	39	39	39

$L = C_{14}H_{11}NO_4$

Table 11: Result of Antifungal Activities of the Schiff Base and Its Metal (II) Complexes

Test Organisms	*Mucor species*			*Aspergillus flavus*		
Concentration (µg/disc)	**60**	**30**	**15**	**60**	**30**	**15**
Ligand	6	6	6	6	6	6
$[CoL_2].2H_2O$	15	13	10	15	13	12
$[NiL_2].2H_2O$	11	8	7	7	6	6
Nystatin	31	31	31	39	39	39

$L = C_{14}H_{11}NO_4$

DISCUSSION

The Schiff base found to be a yellow crystalline product with a good yield of 73.6% and a melting point of 185^{o}C. The metal complexes of Cobalt (II) and Nickel (II) were found to be pale brown and light green crystalline prodocts with a yield of 88.6%, and 76.9% respectively. The decomposition temperature of both Ni (II) and Co (II) complexes were found to be 285 and 270 ^{o}C respectively, this suggests a good thermal stability and it is in agreement with work of [7].

Solubility of the Schiff base and corresponding metal complexes were also determined in different solvents. The Schiff base was found to be insoluble in water, ethanol and acetone but soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). Likewise, all the complexes are insoluble in water but soluble in DMSO and DMF. Both Schiff base and the complexes were found to behave differently in other solvents as presented in Table 2.

The molar conductance measurement of the complexes was carried out in 10^{-3} M of DMSO and the values were found to be in the range of 6.5 and 25.9 $\Omega^{-1}cm^2$ Mol^{-1} (Table 3). The values obtained were low – suggesting that, the complexes are non-ionic, therefore non-electrolytes, and this agrees with work of [8].

The bonding formation between the Schiff base and metal (II) ions were studied by comparing the IR spectrum of free Schiff's base with that of the complexes. The infrared spectral result of the Schiff base showed vibrationl peak at 1574 cm^{-1} in the spectrum of the ligand which was absent in the spectrum of the starting aldehyde and amine materials. This new band at 1574 cm^{-1} can be assigned to the azomethine band (-C=N-). However, it was observed to shift in the spectra of the metal complexes of Ni (II) and Co (II) to 1538 – 1592 cm^{-1} respectively. The shift in the frequency might suggest that azomethine nitrogen have been involved in the coordination with the metal ion. Furthermore, two new peaks were observed in the spectrum of the complexes, one in the range of 670 – 694 cm^{-1} and the other within the 694 to 764 cm^{-1} range, the new peaks were assigned to the corresponding metal–oxygen and metal–nitrogen bonds respectively. The results are presented in Table 5.

The magnetic moment values of the complexes obtained are in the range of 1.79-5.63 BM, (Table 4). The values suggested that the complexes are paramagnetic in nature. Metal ions in the complexes exhibit paramagnetic and diamagnetic properties due to the presence of unpaired electron(s) or absence of it respectively in the orbital of the metals [9]. The percentage composition of the metal was found in the complexes gravimetrically. The result obtained was in good agreement with calculated values. The percentage of the ligand was determined by difference and the results obtained were within the calculated values as presented in Table 6. The percentage of water of crystallization in the complexes was determined and the result showed that Co (II) and Ni (II), complexes contained 7.85% and 7.30 % water respectively (Table 9) The empirical formulae of the metal (II) complexes were determined from the % compositions of the metal (II) ions, water of crystallization and the ligand. The results obtained suggested the general formula $[ML_2]. nH_2O$. Where M = $Ni2^+$ and $Co2^+$, as presented in Table 9 [10].

Determination of metal: ligand ratio was done using Job's method of continuous variations. The result showed a metal:ligand ratio of 1:2 as presented in Table 7. The result is in agreement with the work of [11]. The biological screening of the Schiff base and its metal (II) complexes were studied against three bacterial and two fungal isolates using disc diffusion method. The bacteria isolated used were *Staphylococcus aureus, Escherichia coli* and *Pseudomonas anginosa* while the fungi are *Mucor indicus* and *Aspergillus Flavus*. Septrin and Nystatin were used as control for the bacteria and fungi respectively. The zones of inhibition (mm) were measured for both the discs. The results of the antibacterial screening of the Schiff base at a concentration of 60mg/ml against all bacteria isolatates studied indicated that the Schiff bases showed significant activity against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* while the complexes were found to be more active against all tested bacterial strains. Antibacterial activity of these compounds increases with increase concentration as presented in Table 10.

The antifungal activity studies of the compound showed that Co (II) have highest activity in both *Mucor indicus* and *Aspergillus flavus* isolates. Ni (II) showed moderate activity while the Schiff base has minimal activity against the isolates (Table 11).

The antimicrobial data reveals that the complexes and the ligand are bioactive because of their activities against these tested microbes. The results of antimicrobial activities were compared with standard drug as positive control their activities were found to be lower than that of the control.

CONCLUSION

Schiff base derived from 4-amino-2-hydroxybenzoic acid with 2-hydrobenzaldehyde and its metal (II) complexes of cobalt and nickel were synthesized. The molar conductance of the complex's values indicated that, the complexes were non-electrolytes. Solubility test results showed that the ligand and the complexes were soluble in DMF and DMSO, but insoluble in distilled water. The melting point and the thermal decomposition temperatures of the Schiff base and complexes were determined, the higher temperatures suggest stability. The magnetic moment values of the complexes obtained suggests the complexes to be paramagnetic. Metal: ligand ratio of 1:2 were determined using Job's method of continuous variations. The biological screening of the Schiff base and its metal (II) complexes were studied and result revealed that the complexes exhibit higher activities than the Schiff base, but lower than the control.

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