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Synthesis and antimicrobial activity of manganese (II), iron (II) and cobalt (II) complexes with schiff base derived from ethylenediamine and 2-hydroxy-1-naphthaldehyde

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ABSTRACT: Three metal complexes of Manganese (II), Iron (II) and Cobalt (II) with Schiff base derived from Ethylenediamine and 2-hydroxy-1-naphthaldehyde were synthesized. The metal complexes were analysed using infrared spectrometry, Mass spectrometry and elemental analysis. The C=N bond was found to be intact, with absorption band at 1626,1628 and 1624 cm^{-1} for Mn (II), Co (II) and Fe (II) respectively. The complexes were found to be stable (decomposition temperature ~316^{0}C). Metal complexes synthesised demonstrated moderate anti microbial against *Escherichia coli* and *Aspergillus nigger*.

Keywords: Schiff base, manganese, iron, cobalt

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INTRODUCTION

Schiff base ligands are easily prepared by condensation of amines and aldehydes, and can easily be modified. This makes them easy access to coordination chemist (Pier 2004). Schiff bases are generally capable of forming very stable complexes with transition metals, They can only act as coordinating Schiff bases if they bear a functional group usually hydroxyl sufficiently near the azomethine in such a way that a five or six member ring can be formed when reacting with a metal ion (Marvin, *et al.* 2002).

Several azomethine derivative (C=N) compounds are believed to have wide application in food industry, dye industry, analytical chemistry, catalysis, agrochemical and as antimicrobial (Genin *et al,* 2000). Metal complexes of Schiff base derived from 2-furancabaxaldehyde, o-phenylenediamine, and 2-thiophenecabaxaldehyde have been synthesized and characterized based on IR, NMR, solid reflectance and thermogravimetric analysis (Mohammed *et al.*, 2006). The complexes were screened for their activity against bacteria and fungi, the result showed metal complexes to be very active against bacterial growth. Several Schiff bases have also been reported to possess anti-inflammatory and allergic inhibitors reducing activity while Salicylidine anthranilic acid copper complex possesses antiulcer activity (Anant and Devjani 2009).

Raman *et al.* (2005) synthesized Schiff base derived from 4-aminoantipyrine and 3-salicylidineacetylacetone and complexed it with transition metal (II) ion. This novel tetradentate N_2O_2 type Schiff base form stable complexes with transition metal ions such as Cu (II), Co (II), Ni (II) and Zn (II) in ethanol, electronic Absorption spectra suggest a square planer geometry around the central metal ion. These complexes show higher

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conductance value supporting the electrolytic nature.

In another report (Florence *et al.* 2001) a metal complex was synthesized, which showed an effect on human immuno deficiency virus type 1 protease (HIV - 1 - pr). The Cu(II) complex ([Di aqua (bis (2-pyridil carbonyl) amido) Cu(II) nitrate di hydrate]) and [Bis (N_2(2,3,6 - tri methoxy benzyl) 4,2 - prydine carboxamide) Cu(II)] behave *as* inhibitors of H1V-I pr. Three different crystal structures were obtained. Two were found to contain ligand (L) simultaneously in a tridentate and bidentate conformation (CuL (tri) and CuL(bi)) the other Contained two symmetry related ligands, coordinated through the prydine nitrogen and the amide oxygen atoms (Cu (L (bi)) (2)). In this paper metal (II) complexes will be synthesized and tested for their anti microbial activity against *Escherichia coli* and *Aspergillus nigger*.

MATERIALS AND METHOD

Experimental Materials

All reagents and chemicals purchased from Aldrich sigma were of analytical/ spectroscopic grade and used without further purification.

Schiff base synthesis (NaphSal)

2.52g of 2-hydroxy-1-naphthaldehyde was dissolved in 50ml methanol contained in a 250ml round bottom flask.0.44g of ethylenediamine was added to the solution, the yellowish mixture was

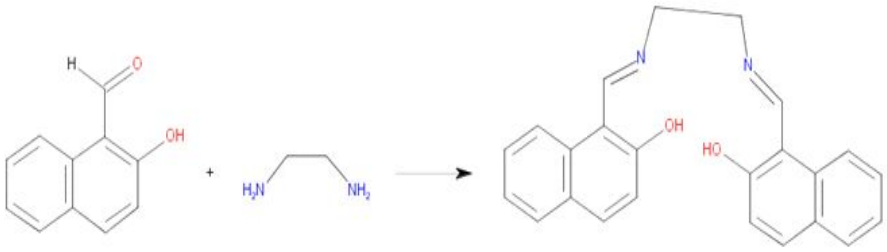

Figure 1: ???????

refluxed for 90 minutes and allowed to cool which form a yellow powder. The yellow powder was collected by filtration. Yield 63 %

Preparation of [FeNaphSal]

0.2326g of Iron (II) chloride tetrahydrate was dissolved in 50ml methanol in a 250ml round bottom flask. 0.44g of NaphSal was added to the solution, the light brown mixture was refluxed for 90 minutes and allowed to cool, the dark brown powder was collected by filtration and then dried. Yield 53%, Anal. Found: C, 68.43; H, 4.42; N, 6.81: Calcd. C, 68.27; H,4.30; N, 6.63: MS (Electron Ionisation; m/e): [M]+ 422.

Preparation of [MnNaphSal]

0.149g of manganese (II) chloride hexahydrate salt was dissolved in 50ml methanol contained in a 250ml round bottomed flask. 0.295g of the ligand was added to the solution, which immediately turns into the light brown mixture. The mixture was refluxed for 90 minutes, then allowed to cool. Then greenish yellow powder was collected by filtration then dried. Yield 53%: Anal. Found: C, 68.61; H, 4.53; N, 6.81: Calcd. C, 68.41; H, 4.31; N, 6.65: MS (Electron Ionisation; m/e): [M]+ 421.

Preparation of [CoNaphSal]

0.121g of cobalt (II) chloride hexahydrate was dissolved in 50ml methanol contained in a 250ml round bottom flask, 0.332g NaphSal was added to the solution which turns to light brown mixture, and was refluxed for 90 minutes and allowed to cool. The brownish powder was collected by filtration and then dried. Yield 73%: Anal. Found: C, 67.11; H, 3.97; N, 7.03: Calcd. C, 67.77; H, 4.27; N, 6.59MS (Electron Ionisation; m/e): [M]+ 425.

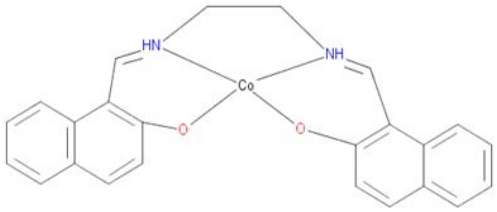

Figure 2: Proposed structure of the metal complexes ([CoNaphSal])

Invitro anti microbial activity

The microorganisms used for this study were obtained from the biological sciences laboratory of Umaru Musa Yar'adua University (UMYU) Katsina. The organisms used were *E-coli,* and *Aspergillus.*

Preparation of the culture medium

Potato Dextrose Agar (PDA) (19.5g) was weighed by the use of electronic top loading balance, distilled water (500ml) was also measured using graduated measuring cylinder. The measured distilled water was poured in borosilicate glass beaker and the measured potato Dextrose Agar was dissolved in it. The mixture was heated over a Bunsen burner flame with continuous stirring until it comes to boil The heat was turned off as soon as it boiled while the hot agar was poured into a clean conical flask. The mouth of the conical flasks containing the media were plugged with cotton wool and placed in an autoclave. The media was sterilized at 1210C for 15 minutes. After sterilization, the conical flasks were removed and cooled to 500 C. The medium was then poured into sterile Petri dishes and allowed to solidify before inoculating. The same procedure was carried out using Nutrient Agar to test the bacterial isolate. (Anacona *et. al.. 2005)*

Antimicrobial activity test

Using disk method

Using sterile inoculation wire loop, bacterial colony was picked from the Test isolate aseptically from the plate and was streaked on the labelled Petri dish containing nutrient agar. Two disks one containing the concentrated complex and the second disk as a negative control were picked and placed on the labelled Petri dish using sterile forceps. The procedure was repeated for the remaining Petri dishes respectively. Small portion of the fungal colony was picked and placed at the centre of the PDA plates by the use of inoculating needle while the disks were placed 2cm each away from the inoculum. The inoculated fungal plates were incubated at room temperature for 1-3 days while bacterial plates were incubated at 370C for 24 hours. The appearance of growth was recorded as activity and non- activity also the zone of inhibition was noted (Mitscher,1982)

Pouring method

To the prepared media, 1ml from each of the serially diluted complex or the Schiff base were pipetted using a sterilized syringe and transferred into a sterilized Petri-dishes followed by the addition of the potato dextrose agar media, the plate were allowed to solidify before inoculating the fungal isolate. The plates were kept at room temperature for 3 days, and the fungal activities were noted.The same procedure was carried out for the bacterial isolate using 28g of the nutrient agar in 1000ml of distilled water.

RESULTS AND DISCUSSION

The complexes derived from 2-hydroxy-1-naphthaldehyde are easily prepared by reacting the ligand directly with the relevant metal salt, *viz;* manganese chloride, cobalt chloride and zinc chloride. The complexes were collected and allowed to dry. These complexes were subjected to spectroscopic analysis which includes infrared spectroscopy and mass spectrometry while solubility test and decomposition temperature were also determined.

The infrared spectral band of the Schiff base observed at 1256 cm^{-1} is assigned to the stretching vibration of the C - O bond. Several literatures have reported the absorption band of the C-O to appear between the range 1340 cm^{-1} -1220cm^{-1} (Ahmed *et al* 2009). The azomethine C=N bond is the fundamental characteristic of all Schiff bases, as such it is accorded priority when looking at the infrared spectra of a Schiff base compound. The presence of the bond in amolecule suggests the formation of the Schiff base ligand, while its persistence in a complex suggest the absence of hydrolysis in the resulting compound. In the spectra of our compounds it appears at1629 cm^{-1} for the ligand. The medium absorption band that appear at 1455 cm^{-1} was due to the stretching vibration of C=C bond in the aromatic ring. The elemental analyses and the mass spectra further confirmed the identities of the three metalcomplexes.

Solubility test and decomposition temperature: The complexes were tested for their solubility in common solvents and their stability with regards to heat, the results are presented in Table 1.

Table 1: Solubility test for the synthesised complexes and the Schiff base

Compound	Ethanol	Chloroform	Benzene	Diethylether	N-hexane	Acetone	Water
Schiff base	Insoluble	Soluble	Soluble	Soluble	Insoluble	Soluble	Insoluble
MnNaphSal	Soluble	Insoluble	Soluble	Soluble	Insoluble	Soluble	Insoluble
CoNaphSal	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble
FeNaphSal	Insoluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble

Decomposition temperature

The decomposition temperature of the complexes ranges between 316^0C-327^0C and this confirm the stability of the complexes.

Activity against microorganism

The complexes were tested against two organisms, namely *Escherichia coli* and *Aspergillus,* which reveals promising result. The culture was allowed for three days after adding the complexes and the growth of the organism was observed. From the results it was found that the complexes have no significant effect on the bacterial growth (*E-Coli*) (Table 2). However, on the other hand the complexes were found to inhibit the growth of the fungi strongly (*Aspergillus*). The growth of *Aspergillus* could not easily be detected until after three days (Figure 2), which probably suggest that within that period the compound was very active and intact, to the level that it could not allow the growth completely of the microorganism. After that period the compound potency is assumed to have started deteriorating such that the growth of the bacteria begins.

Table 2: antimicrobial (zone of inhibition) (cm) activity of the complexes against the microorganisms per concentration

Complex	Isolates	10^{-1}µg/ml	10^{-2} µg/ml	10^{-3} µg/ml	10^{-4} µg/ml	10^{-5} µg/ml
NaphSal	*E-Coli*	0.40	0.30	0.25	0.20	0.10
	Aspergillus	0.60	0.52	0.45	0.42	0.30
MnNaphSal	*E-Coli*	0.35	0.32	0.30	0.20	0.15
	Aspergillus	0.40	0.80	0.53	0.62	0.50
CoNaphSal	*E-Coli*	0.52	0.49	0.45	0.40	0.30
	Aspergillus	0.90	0.58	0.45	0.40	0.50
FeNaphSal	*E-Coli*	0.40	0.35	0.30	0.28	0.23
	Aspergillus	0.75	0.70	0.58	0.60	0.55

CONCLUSIONS

Metal complexes of Manganese (II), Iron(II) and Cobalt(II) with Schiff base derived from Ethylenediamine and 2-hydroxy-1-naphthaldehyde has been successfully synthesized, the complexes were found stable with decomposition temperature of 316^{0}C and 326^{0}C. From the antimicrobial test carried on these compounds it is evident that the compounds are more active against the fungi. Further work could be carried out on these complexes, by attaching a substituent on the ligand phenyl ring and then investigate their activities.

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