Synthesis, Characterization and Antimicrobial Evaluation of Mixed Ligand Complexes of Dimethiglyoxime and Barbitone with Nickel (II) Ions in Water-Methanol Medium

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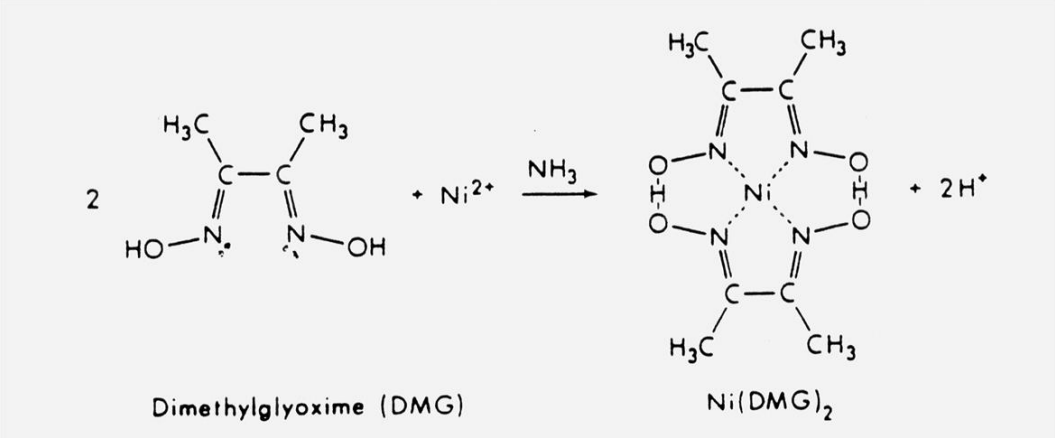
Abstract- ***Mixed ligand complexes of Dimethyglyoxime (DMG) and barbitone with Nickel (II) ion in water-methanol medium at different ratio concentration were carried out by direct mixing method. The synthesis of Ni(II) complexes with DMG and Babitone were characterized on the basis of physical properties such as colour,% yield, melting point and % metal analysis using complexometric titration method and as well as spectroscopy data of analysis which include the UV-Visible and FTIR-Spectroscopy. The result of physical properties of the Ni (II) complexes revealed that the metal complexes were pure, non-hygroscopic in nature with sharp melting points and reasonable percentage yields. The solubility tests result showed that Ni (II) Dmg complexes and its mixed ligand were non-electrolyte and non-polar in nature. The spectroscopic results presumed that coordination of Ni (II) to the free ligand DMG was through the oxygen atom of oxime and nitogen atom of Barbitone mixed ligand. The results of anti-microbial analysis predicted that mixed ligand complexes performed fairly against the selected pathogens while the ligands were totally inactive.***

Key word: Mixed ligand , Dimethylglyoxime, barbitone, Nickel(II).

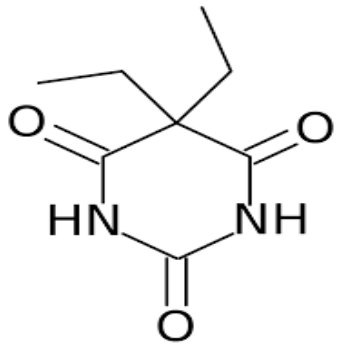
I. INTRODUCTION

Mixed ligand complexes are distinct from conventional complexes in that they contain a minimum of two distinct ligand types linked to the same metal ion by complexation. Numerous researchers have become active in this discipline as a result of the growing interest in drug resistance pathogens [11].

Dimethylglyoxime is a chemical molecule that is soluble in methanol and was one of the first selective organic reagents used in analytical techniques for spectroscopic determination of nickel as nickel (II) dimethylglyoxime complex. Dimethylglyoxime is a bidentate ligand with two donor atoms through which it can coordinate to form stable metal chelate with metal ions [10].Nickel cation reacts with dimethylglyoxime and forms an insoluble red precipitate of nickelglyoxime,it also react with ferrous salt and ammonium hydroxide to form a complex compound of iron and ammonium. Dimethylglyoxime is also used as a test for nickel and a precipitating agent for nickel and palladium [8]



Barbitone, sometimes referred to as barbiturate, is a derivative of barbituric acid (2,4,6-trioxopyrimidine). Due to the numerous medicinal uses of barbitone, the medication has a variety of uses, including hypnotics, sedatives, anesthesia, anticonvulsants, and the treatment of anxiety, epilepsy, and other mental disorders [13].



Barbitone

Barbitone metal complexes have been reported to coordinate bidentately through the oxygen of the carbonyl group and nitrogen atom of the amine in the ring, also the result of biocidal evaluation proved that barbitone metal complexes were suitable for bacterial and fungal eradication [12]. In this study, mixed ligand complexes of barbitone and dimethylglyoxime with nickel (II) ion in water-methanol medium were synthesized, characterized and the antimicrobial activities evaluated.

II. MATERIALS AND METHOD.

All reagents used were of analytical grade. All chemicals were obtained from sigma-Aldrich. All the reagents and solvents were purchased commercially and used. The melting points were recorded in melting point apparatus. The Infrared spectra were recorded by using FTIR8300 Shimadzu spectrophotometer in the frequency range of 4000 - 400cm^{-1}.The (UV-vis) spectra were recorded using Shimdzu UV-VIS.

SYNTHESIS OF NICKEL (II) COMPLEXES.

Equimolar concentrations of the metal salt of 0.59g $NiCl_2.6H_2O$ and 0.35g Dimethylglyoxime were carefully weighed, dissolved and homogenized in 10ml distilled water and 10ml methanol and were prepared in ratio 1:1. The mixture was stirred on a magnetic stirrer continuously for 3hrs as resulting mixture gave red. This process was repeated for ratio 1:2. The resulting mixture was filtered through a sintered glass in a porosity number 4 and dried in a desiccator containing silica gel for five days until constant weight achieved.

The mixed ligands complexes were also synthesized by weighing equal concentration of the metal salt $NiCl_2.6H_20$,Dimethylglyoxime and Barbitone dissolved in ratio 1:1:1 and ratio 1:2:1. The process of filtration, washing, drying and weighing followed the above step [12]

ANTIMICROBIAL STUDIES OF METAL COMPLEXES

All novel synthesized complexes were tested for their antibacterial activities against the selectected bacteria ; *Salmonella typhi(typhoid fever causative agent), Ralstonia solanacearum, Streptococcus faecalis , Erwinia carrrotovora and Pseudomonas glycinea* and anti-fungal activity against *Serpula lacrymans, Epidermophyton floccosum and Trichophyton verrucosum* .The control tube containing no antibiotic is immediately sub-culture by spreading a loophole evenly over a quarter tube of plate of medium suitable for the growth of the test organisms and put for incubation at 37ºC overnight. The MIC (Minimum inhibitory concentration) of the control organism is read to check the accuracy of the drug concentration [8]

III RESULTS AND DISCUSSION

PHYSICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF NI (II) WITH DMG AND BARBITONE.

Metal complexes of Ni (II) with dimethylglyoxime and its mixed ligand barbitone gave different colours. The variation in the colour of metal complexes from the ligand is an indication of d-d electronic transition initiated by the promotion of electron from one energy level to another, being caused by dominant effect of the ligands on the Ni (II) central metal ions. The dominant effect of the ligand (DMG) on Ni (II) changed green to pink and the mixed ligand DMG and Barbitone also responsible for light green recorded for the mixed ligand complexes. The percentage yields of the free ligand and its mixed ligand were high, reasonable and commendable. The melting points or decomposition temperature of the NI (II) mixed ligand complexes were found between 185-187ºC for the free ligand and 245-247ºC for the

mixed ligand. The sharp melting points recorded so far indicated that metal complexes are pure, single, non - hygroscopic solids with melting point higher than melting points of standard ligands as shown in table 1.0 [1][4]

Table 1.0: PHYSICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF NI (II) WITH DIMETHYLGLYOXIME (DMG) AND BARBITONE

COMPOUND	RATIO	COLOUR	%YIELD	M.P.t/decomposition temperature	%METAL
[NI(DMG)H_2OCL].5H_2O	I:1	Red	52..69	244-246ºC	12.63
[NI(DMG)$_2$$H_2$OCL].5$H_2$O	1:2	Red	60.54	245-247 ºC	13.33
[NI(DMG) (Barb)H_2OCL].5H_2O	1:1:1	Light -green	41.49	185-187 ºC	11.94
[Ni(DMG)$_2$(Barb)H2OCL].5H2O	1:2:1	Light-green	49.63	225-227 ºC	10.67
BARBITONE		white			
DIMETHYLGLYOXIME(DMG)		wine			

Table 1.1: SOLUBILITY TEST

Complexes	DMSO	Toluene	Methanol	Ethanol	Chloroform	DMF	Ethyl ethanoate
[NI(DMG)H_2OCL].5H_2O	SS	SS	IS	IS	IS	SS	IS
[NI(DMG)$_2$$H_2$OCL].5$H_2$O	SS	SS	IS	IS	IS	IS	IS
[NI(DMG) (Barb)H_2OCL].5H_2O	SS	SS	IS	IS	IS	SS	IS
[Ni(DMG)$_2$(Barb)H2OCL].5H2O	SS	SS	IS	IS	IS	IS	IS

SS = soluble IS = insoluble

The solubility of metal complexes were examined on the following transparent organic solvents. These include, toluene, methanol, ethanol, chloroform, Dimethylformadehyde and ethyl ethanoate .Metal complexes were soluble in DMSO, Dimethyl formaldehyde (DMFA) and toluene this indicates that complexes were non-polar in character. This result paves way for UV-Visible spectroscopic studies of metal complexes as Uv-visible spectroscopy is solubility dependent as shown in table 1.1.

Table 1.2: UV/VISIBLE SPECTROSCOPIC STUDIES OF MIXED LIGAND COMPLEXES OF Ni (II) DIMETHYLGLYOXIME (DMG) AND BARBITONE (Barb) COMPLEXES

DMG (λ)nm	ABS	BARB (λ)nm	ABS	NiL1:1 (λ)nm	Abs	NiL1:2 (λ)nm	Abs	NILL1:1:1 (λ)nm	ABS	NILL1:2:1 (λ)nm	ABS
682	0.123	763	0.137	762	0.249			762	0.031	678	0.267
648	0.087	680	0.159	678	0.327	680	0.174	673	0.055	562	0.142
				584	0.276	564	0.183				
404	0.010	427	0.010					492	0.010	571	0.239
386	0.011	367	0.010			358	0.005	296	0.028	296	0.038
				296	0.043	294	0.035				
253	0.031	256	0.039	253	0.042	253	0.038	259	0.030	253	0.038

The electronic transition spectra of the ligands and the metals complexes with the significant absorption bands were given in table 1.2. In the electronic spectra of dmg the maximum absorption band which appeared at λmax .682nm and absorption at 0.132 and λmax.252nm at 0.031 absorbance were assigned to π--π* and n—π respectively. These transitions π--π* and n—π can be attributed to carbonyl and amine moiety in the ligand [12]. These electronic transition were also occurred in the spectra of the metal complexes, but found to be shifted towards higher or lower frequencies in both Ni (II) Dimethylglyoxime and its mixed ligand [15]. These differences in transition in the metal complexes revealed the coordination of the ligands to the nickel (II) ions mainly caused by ligand-metal charge (LMCT) or metal –ligand charge transfer (MLCT). The spectra of Ni(II) complexes Ni(dmg) and Ni (dmg)(Barb)

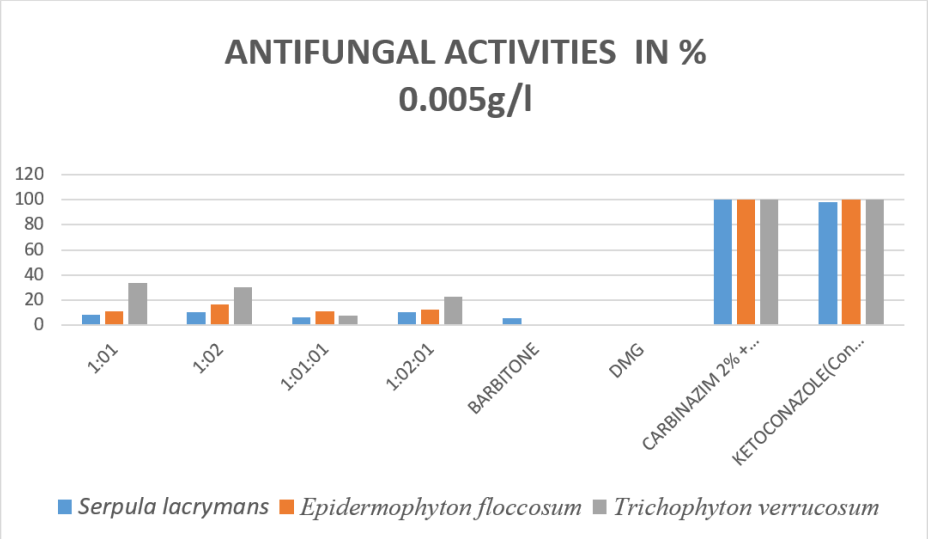
display two d-d transitions which might ascribe to $^3T_{ig}(F) \rightarrow {}^3A_{2g}$ and $^3T_{2g}(F) \rightarrow {}^3A_{2g}$ respectively. These band assignments indicated a nearly tetrahedral environment around the Ni (II) ion complexes [13].

Table 1.3: SUMMARY OF THE RELEVANT PROMINENT REGIONS OF FTIR FOR THE LIGANDS AND METAL COMPLEXES OF NI (II) (DMG) (BARBITONE)

Compound	(C=N)	(N-O)	(C=O)	C-O	N-H	M-N	M-O	(O-H)
Dimethylglyoxime	1435	1133			-			3207
Barbitone	1042,1056		1636	1056	3058 3182			-
1:1	1435	1143				520	464	3206,3660,37117
1:2	1438	1143				520	464	3209,3660,3786
1:1:1	1430,1571	1100,1239	1699,1799	1100	3241	519	469	3208,3696
1:2:1	1493,1572	1101,1239,1173	1677,1765,1765	1101,1083	3226,3081	519	457	3209

The FTIR spectra of the metal complexes showed peaks resemble those of the ligands (dmg) and (barbitone) but with slight differences. The v(C=N) strong band at 1435cm^{-1} in free ligand (DMG) was observed also at nearly the same frequencies in the spectra of metal complexes around 1435,1438,1430,1493cm^{-1}.This suggests that metal coordination to ligand may not likely occur through the nitrogen atom of the oxime [2][11].The appearance of single strong band at 1133cm^{-1} in dmg shows that two oxime group are identical while the appearance of a band for the complexes at around 1100-1143 is assigned to (N-O).This shows that Ni(II) ions may likely be coordinated through the oxygen atom of the oxime .Also ,another prominent single band found at 3207cm^{-1} for the dmg ligand but shifted to higher bands in all metal complexes. This shift to higher band is attributed to hydrogen bridges between the dimethylglyoxime (dmg) [9].The mixed ligand complexes displayed different band apart from the ligand. The (N-H) bands of barbitone ligands around 3058, 3183cm^{-1} with a bathochromic shifts in all the metal complexes with band frequencies around 3241, 3226 and 3081cm^{-1} confirms the coordination of metal ions through the nitrogen atom of the amide group. However, a conspicuous band at 1056cm^{-1} in the spectrum of Barbitone (ligand) ascribe to (C-O) has witnessed a shift to higher wave number in the spectra of the metal complexes of the mixed ligand to 1100,1101,1083cm^{-1} respectively .This demonstrates the coordination of nickel(II)ions through oxygen atom of oxime. The (M-N) and (M-O) bands observed at 519-520 cm^{-1} and 457-460cm^{-1} also confirmed the Ni(II) ions coordination through the nitrogen and oxygen atoms bidentately [3]

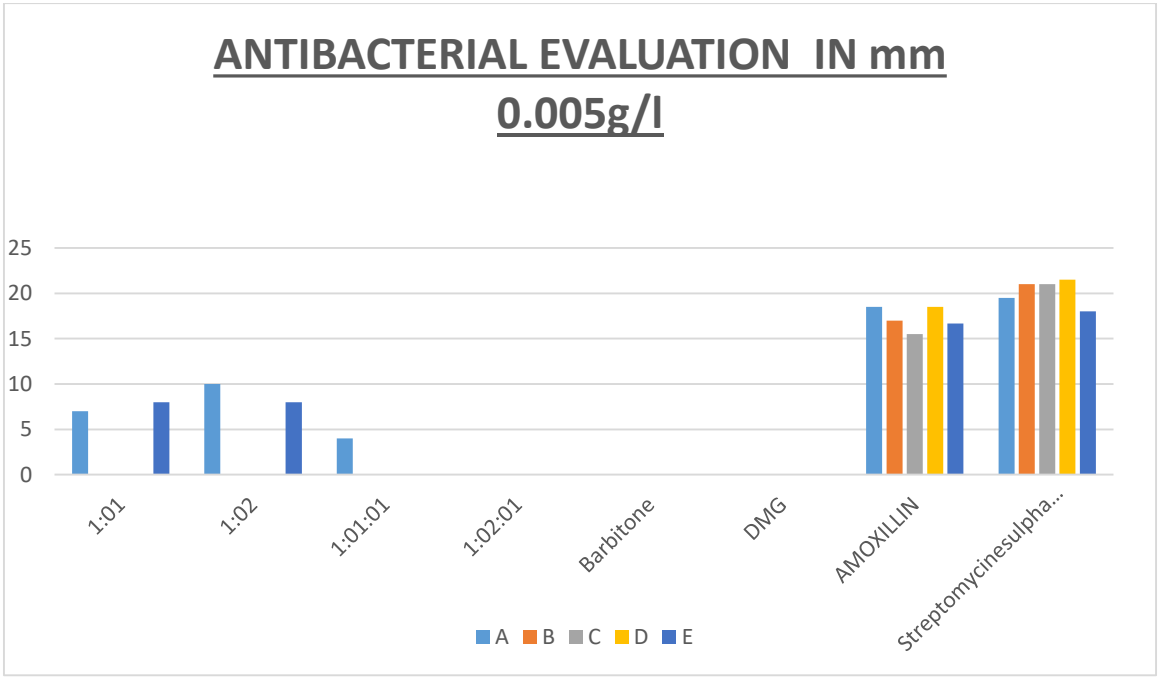
Figure 1.1: Antifungal activities of mixed ligand complexes of NI (II) With DMG and Barbitone



1:1 = [NI (DMG) H_2OCl] .$5H_20$, 1:2 = [Ni $(DMG)_2$ H_20Cl].$5H_2O$
1:1:1 = [Ni (DMG) (Barb) H20Cl].5 H_2O, 1:2:1 = [NI $(DMG)_2$(Barb) H_20Cl].$5H_2O$
DMG =Dimethylglyoxime.

The results of the antifungal activities of the metal complexes against some selected fungi revealed that the metal complexes of Ni (II) ions with the free ligand and its mixed ligand performed fairly on the selected organism. Mixed ligand complexes at different ratio concentrations performed below expectation this may due to the effect of barbitone ligand which it is supposed to increase the inhibitory actions of the complexes. The free ligand (dmg) performed poorly but upon complexation with Ni(II) ions that is Ni(dmg) in ratio 1:1 and 1:2,the performance against *Trichophyton verrucosum is* better at 33.69 and 30.43% inhibition compare to other oganisms while the rest two organism showed resistance against complexes. It is envisaged that the antifungal activity of the metal complexes may be improved by increasing the concentration of the ligand [9] [13].

Figure 1.2: Antibacterial evaluation of mixed ligand complexes of NI (ii) with DMG and Barbitone



1:1 = [NI (DMG) H_2OCl] .$5H_20$, 1:2 = [Ni $(DMG)_2$ H_20Cl].$5H_2O$
1:1:1 = [Ni (DMG) (Barb) H_20Cl].5 H_2O, 1:2:1 = [NI $(DMG)_2$(Barb) H_20Cl].$5H_2O$
DMG =Dimethylglyoxime.
A = *Ralstonia solanacearum, B = Salmonella typhii C = Streptoccum faecalis. D = Erwinia carotovoria, E = Pseudomona glycinea.*

The results of antibacterial activity of the metal complexes, the free ligand and the mixed ligand were not encouraging. The two ligands did not show any sign of inhibition while the reference and the control (antibacterial) performed with significant zone of inhibition .The metal complexes showed a little signs of inhibition against *Ralstonia solanacearum* and *Pseudomona glycinea*. This shows that metal complexes of Ni (II) dmg could be recommended as a drug for diseases caused by those organisms.

IV CONCLUSION

Mixed ligand complexes have been successfully synthesized and characterized by both physical and spectroscopic techniques. The variation in the colours of the Nickel (II) complexes at different ratio showed that the ligands have dominant effects on the metal ions. The mixed ligand complexes of Nickel (II) (DMG)(Barb) were stable and non-polar in metals. Nickel (II) ion is believed to have coordinated through the oxygen atom of the oxime and nitrogen atom of the barbitone mixed ligand .All the

synthesized metal complexes performed fairly on all selected pathogens compared to both the free ligand and mixed ligand.

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