

Full Length Research Paper

# Synthesis, physico-chemical and antimicrobial properties of Co(II), Ni(II) and Cu(II) mixed-ligand complexes of dimethylglyoxime - Part I

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Some mixed-ligand complexes of the general formula  $[M(\text{Hdmg})_2\text{B}]$ , where Hdmg = dimethylglyoximate monoanion, B = 2-aminophenol, diethylamine or malonic acid were prepared. The complexes were characterized by metal analysis, melting points, solubility, conductivity, infrared and UV/VIS electronic spectra. The antimicrobial activities of the complexes were tested using *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Aspergillus flavus*. The complexes melted/decomposed at 120 - 306°C and, most of them dissolved only in polar solvents. The complexes are mostly dark-brown or black. The IR spectra indicated that the complexes coordinated, through the N atom of the oxime group of Hdmg, and O atoms of the 2-aminophenol or malonic acid. In the electronic spectra of the complexes, the absorption bands observed in the UV/VIS region are presumed to be either due to charge transfer or intra-ligand transitions from the ligands or d-d transitions from the metal ions. The complexes showed antimicrobial activity against the tested micro-organisms at 10 mg/ml. The possible use of the complexes as antibiotic can therefore be suggested.

**Key words:** Dimethylglyoxime, UV/Visible spectroscopy, infrared spectroscopy, antimicrobial activities.

## INTRODUCTION

Much attention has been paid to the studies of mixed-ligand complexes of metals in recent years because of their wide application in various fields of chemical activity and more particularly because of their presence in biological, environmental and other systems (Khanol et al., 1973; Bruce and Ronaldo, 1974; Ramanujam and Krishnan, 1981).

In fact, many naturally occurring metal complexes are mixed-ligand complexes (Perring and Aggarwal, 1973) containing two or more different ligand molecules, or if the ligand is a single macromolecule having two or more different kinds of donor atoms (Bruce and Ronaldo, 1974). Furthermore, mixed-ligand complexes are generally found to be more active biologically than the ligand itself and its binary complexes (Malik et al., 1977). From literature, some workers (Kudirat et al., 1994; Yeamin et

al., 2003; Canpolat and Kaya, 2004; Peter and Kolawole, 2005) have reported the use of metal complexes in fighting microbial infections.

This paper reports the synthesis of mixed-ligand complexes of some first row transition metal ions using dimethylglyoxime as primary ligand and 2-aminophenol, diethylamine or malonic acid as secondary ligands. The activity of the ligands and the complexes against *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger*, and *Aspergillus flavus* were also studied.

## MATERIALS AND METHODS

All reagents and solvents used were of analytical grade. The complexes were prepared according to a modification of literature procedure (Schnauzer, 1968; Kolawole and Ndahi, 2004). The metals were analyzed by complexometric methods (Vogel, 1971). The infrared spectra were recorded on a Genesis II FTIR spectrophotometer in the range 4000 - 450  $\text{cm}^{-1}$  (KBr discs) at the Advance Laboratory, Sheda Science and Technology Complex (SHESTCO), Sheda, Abuja. The electronic absorption spectra of

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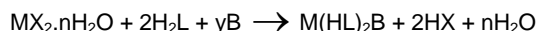
the complexes were obtained with a Shimadzu UV-16A UV-Visible spectrophotometer in DMSO solutions in the range 200 – 800 nm at NIPRD (National Institute for Pharmaceutical Research and Development) IDU, Abuja.

The conductivity measurements were performed at room temperature (32.7°C) using an electrolytic conductivity set, Crison Conductimeter 522, with a cell constant of 1.52 on the complexes that were soluble in either methanol or DMSO at a concentration of  $10^{-3}$  moldm<sup>-3</sup>. Melting points/decomposition temperatures (M.P./D.T.) were measured using Griffin melting point apparatus. The solubility of the complexes was determined in some polar and non-polar solvents. The *in vitro* antimicrobial properties of the complexes were performed in Plant Pathology Laboratory, Department of Crop Protection, University of Maiduguri, using disc diffusion method (Yeamin et al., 2003).

### Preparation of the complexes

The metal complexes were prepared by mixing a solution of the ligand, Hdmg (6 mmol, 0.6970 g) in 80 ml of boiling EtOH with 3 mmol, (0.8731, 0.7466 and 0.5980 g) of the appropriate metal (II) salt dissolved in 20 ml of distilled water. The mixture was magnetically stirred for about 1 h after which 3 mmol of the secondary ligand: 0.3274 g (2-aminophenol), 0.3122 g (malonic acid) dissolved in 20 ml of ethanol was added with magnetic stirring to each preparation. This was refluxed for another 1 h. For diethylamine, 6 mmol. (0.62 ml) was used.

Precipitates were formed within the refluxing time for majority of the complexes, while some required concentration of the colour mixture on a water bath and cooling. Before solid products were obtained. The products were filtered and washed with 3 X 5 ml portions of 50% ethanol/water mixture and then with 2 X 5 ml portions of ethanol. The products were dried in a desiccator over CaCl<sub>2</sub>. The general equation for the formation of the complexes is shown below:



Where M = Co(II), Ni(II) or Cu(II); X = NO<sub>3</sub>, OAc; HL = Hdmg; B = 2-aph, dea or MOH; y = 1 or 2; n = 1 or 6

### Antimicrobial test

The antibacterial and antifungal activities of the complexes were determined by previously described method (Robert and Ellen, 1988; Obaleye and Famurewa, 1989; Taura et al., 2004). Nutrient Agar (NA) and Potato Dextrose Agar (PDA) were used as bacteriological and fungal media respectively. The complexes were dissolved separately in DMSO to get a concentration of 1 and 10 mg/ml per disc. Plating and inoculation were carried out by established procedure (Taura et al., 2004).

In order to determine the antifungal activity of the various compounds, known concentrations of the samples were incorporated into the PDA. The inoculation method described by Manavathu et al. (1988) was used. DMSO was used as the solvent for preparation the different concentrations (1 and 10 mg/ml) of the various compounds. The bacterial and fungal cultures were incubated at 37°C for 48 and 72 h respectively.

The antibacterial activities of the substances were interpreted as resistant or sensitive following the interpretative chart of the Kirby-Bauer sensitivity methods (Cheesbrough, 2000). The inhibition of the fungal growth, expressed in percentage, was determined on basis of the average diameter of the colony compared to the respective control cultures.

$$\% \text{ Inhibition} = \frac{(C - T) \times 100}{C}$$

Where C = diameter of the fungus colony in the control plate; T = diameter of the fungus colony in the treated plate, after three days.

Experimental conditions were maintained as uniform as possible by testing all the twelve samples at the same time using the same culture of the test organisms within the specified period of time.

## RESULTS AND DISCUSSION

The solubility of the complexes in the six solvents used, varied according to divalent metal used: all Co(II) complexes were soluble in water, and methanol except [Co(Hdmg)<sub>2</sub>(dea)<sub>2</sub>]. However all were soluble in DMSO; the Ni(II) complexes were soluble in all the solvents except in water. However, [Ni(Hdmg)<sub>2</sub>], [Ni(Hdmg)<sub>2</sub>(2aph)], and [Ni(Hdmg)<sub>2</sub>(dea)<sub>2</sub>] were insoluble in all the solvents except in DMSO and [Cu(Hdmg)<sub>2</sub>l(dea)<sub>2</sub>] which, in addition, is soluble in methanol.

The complexes exhibit various shades of colour: those of Co(II) complexes were brown except [Co(Hdmg)<sub>2</sub>(dea)<sub>2</sub>] that was black maureen; Ni(II) complexes were red and those of Cu(II) were black, grey-ash and light green. The melting points/decomposition temperatures (M.P./D.T.) complexes are shown in Table 1. Some are sharp and range within 130 - 304°C. Some however decomposed before melting.

On the basis of the analytical data (Table 1), the general formula of the complexes may be proposed as [M(Hdmg)<sub>2</sub>(B)<sub>y</sub>], Where M = Co(II), Ni(II) or Cu(II); B = 2aph, dea or MOH; y = 1 or 2.

The molar conductance values of the complexes in DMSO at  $10^{-3}$  moldm<sup>-3</sup> are in the range 0.05 – 0.17 Ω<sup>-1</sup>cm<sup>2</sup>/mol and this suggests that the complexes are non-electrolytes. Based on the general equation proposed for the metal complexes prepared the dimethylglycinato group acts as monoanion (Adkhis et al., 2000). The other secondary ligands were neutral and except for diethylamine which acts as a monodentate ligand, other ligands were assumed to be bidentate as shown in Figure 1: 2aph coordinating through the oxygen (and perhaps in addition) through the amino group and; the MOH coordinating through one of the oxygen atoms of the carboxylate group (Nakamoto, 1986). One molecule of water is assumed to have coordinated to the metal complexes containing MOH.

The metal analysis of the complexes is consistent with the calculated results from the empirical formula of each compound (Table 1).

### Spectra properties of the complexes

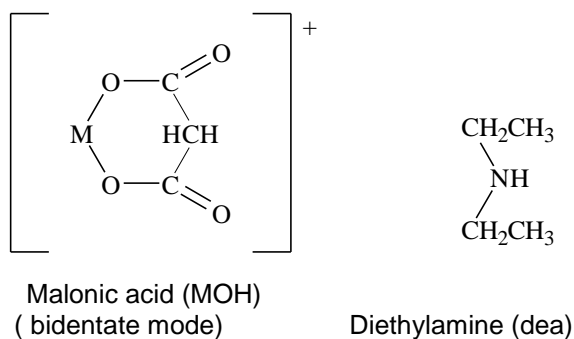
#### Infrared

In order to understand the mode of bonding and the effect of the metal ion on the ligand, the IR spectra of the

**Table 1.** Some physical properties of the mixed-ligand complexes.

Compound	Molecular formulae (molar mass)	Colour	M.P./D.T. (°C)	Yield (%)	$\Lambda_m \Omega^{-1}$ ( $/\text{cm}^2/\text{mol}$ )	% M found (Calculated)
[Co(Hdmg) <sub>2</sub> ]	CoC <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> (289.17)	Light Brown	110 – 112 (d)	63.5	0.17	19.91 (20.38)
[Co(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	CoC <sub>14</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (416.30)	Dark Brown	130	68.2	0.18	15.13 (14.80)
[Co(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	CoC <sub>16</sub> H <sub>36</sub> N <sub>6</sub> O <sub>4</sub> (435.45)	Black Maureen	220 – 250 (d)	27.6	0.04	13.53 (13.53)
[Co(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	CoC <sub>11</sub> H <sub>18</sub> N <sub>4</sub> O <sub>9</sub> (409.23)	Dark Brown	240	78.3	0.12	15.13 (14.40)
[Ni(Hdmg) <sub>2</sub> ]	NiC <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> (288.93)	Rose red	300 – 302 (d)	96.1	0.10	19.80 (20.30)
[Ni(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	NiC <sub>14</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (416.06)	Dark Rose red	304	66.7	0.07	14.70 (14.12)
[Ni(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	NiC <sub>16</sub> H <sub>36</sub> N <sub>6</sub> O <sub>2</sub> (435.21)	Red	302	66.1	0.07	13.48 (13.48)
[Ni(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	NiC <sub>11</sub> H <sub>18</sub> N <sub>4</sub> O <sub>9</sub> (408.99)	Brownish Red	304 – 306 (d)	71.4	0.07	15.07 (14.30)
[Cu(Hdmg) <sub>2</sub> ]	CuCoH <sub>14</sub> N <sub>4</sub> O <sub>4</sub> (293.78)	Black	220 – 230 (d)	66.0	0.07	21.45 (21.63)
[Cu(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	CuC <sub>14</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (420.91)	Grey-ash	200 – 202 (d)	15.87	0.05	15.46 (15.09)
[Cu(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	CuC <sub>16</sub> H <sub>36</sub> N <sub>6</sub> O <sub>4</sub> (440.06)	Black	204 – 208 (d)	10.92	0.05	14.60 (14.4)
[Cu(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	CuC <sub>11</sub> H <sub>18</sub> N <sub>4</sub> O <sub>9</sub> (413.84)	Light-green	206	54.88	0.05	15.70 (15.35)

D = Decomposition temperatures, M = Co(II), Ni(II), or Cu(II).

**Figure 1.** Structural representation of the secondary ligands used in the synthesis.

free ligand and the metal complexes were studied (Table 2) and assigned on the basis of a careful comparison of their spectra with that of free ligand and also from literature reports of similar compounds. The first series for each of the divalent metal complex namely: [Co(Hdmg)<sub>2</sub>], [Ni(Hdm)<sub>2</sub>] have been reported by Burger et al. (1995).

The present bands observed for the various moieties are in close agreement with those they reported for these compounds. The absorption band at 1454  $\text{cm}^{-1}$  in the spectrum of free H<sub>2</sub>dmg has been attributed to  $\nu(C=N)$  group. This band undergoes bathochromic shift to 1461 – 1463  $\text{cm}^{-1}$  in all the mixed-ligand complexes. This is a consequence of the coordination of the metal ion to the dimethylglyoximato monoanion (Adkhis et al., 2000). The  $\nu(N-O)$  stretching frequencies absorb strongly at 1142  $\text{cm}^{-1}$  in the ligand and are shifted to 1154 -1298  $\text{cm}^{-1}$  in the complexes. This could be due to a change in the orientation of N-O bond with respect to H in the ligand and complexes.

In all the complexes, the  $\nu(O-H)$  bond due to O...H – O hydrogen bridges in the ligand is assigned at 3203 – 3477  $\text{cm}^{-1}$  and they all appear as very broad bands. These observations are in agreement with those observed by Adkhis et al. (2000, 2003) even though the metal used was Co(III). In close association with the  $\nu(C-N)$  of H<sub>2</sub>dmg, the band appearing in the 1377  $\text{cm}^{-1}$  of 2-aph and dea respectively were shifted to 1376 -

**Table 2.** Relevant infrared frequencies ( $\text{cm}^{-1}$ ) for the ligands and the complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{O})$	$\nu(\text{N}'-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}'-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{COO}')$	$\nu(\text{C}-\text{O})$	$\nu(\text{NH})$	$\nu(\text{NH}_2)$	$\nu(\text{O}-\text{H})$
2-aph	1377 s 1281 m	-----	-----	-----	-----	-----	-----	1216 sh	-----	3304 sh 3374 sh	3490 sh
Dea	1385 sh	-----	-----	-----	-----	-----	-----	-----	3102 w	-----	-----
MOH	----- 1454 vs	----- 1142 s	----- 977 vs 902 vs	-----	-----	-----	1680 br	1307 m	-----	-----	2942 br
H <sub>2</sub> dmg	1461 s	1237 m	1098 m 1050 m	506 m	-----	-----	-----	-----	-----	-----	3228 br
Co(Hdmg) <sub>2</sub>											3427 br
CoHdmg <sub>2</sub> (2aph)(H <sub>2</sub> O)]	1461 vs	1168 w	1073 m	502 w	-----	722 s	-----	-----	-----	3158 w	3349 br
Co(Hdmg) <sub>2</sub> (dea) <sub>2</sub>	1462 vs	1209 s	1084 s	510 s	-----	-----	-----	-----	3154 w	-----	3410 br
Co(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	1462 m	1164 w	1083 w	509 s	-----	707 w	1605 m	1376 w	-----	-----	3203 br
Ni(Hdmg) <sub>2</sub>	1461 vs	1239 s	1100 m	494 s	-----	-----	-----	-----	-----	-----	3453 br
Ni(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	1462 vs	1239 s	1100 s	520 s	-----	722 s	-----	-----	-----	3244 w	3443 br
Ni(Hdmg) <sub>2</sub> (dea) <sub>2</sub>	1462 vs	1239 s	1100 s	520 s	-----	-----	-----	-----	3218 w	-----	3443 br
Ni(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	1461 s	1239 s	1100 s	502 s	-----	722 m	1572 m	1377 s	-----	-----	3462 br
Cu(Hdmg) <sub>2</sub>	1461 vs	1208 s	1032 s	508 s	450 s	-----	-----	-----	-----	-----	3401 br
Cu(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	1461 vs	1297 s	1027 s	525 s	420 s	620 s	-----	-----	-----	3254 m	3441 br
Cu(Hdmg) <sub>2</sub> (dea) <sub>2</sub>	1463 vs	1197 m	1096 m	521 w	487 s	-----	-----	-----	3249 w	-----	3431 br
Cu(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	1461 s	1230 m	1061 w	508 m	-----	723 s	1573 m	1377 s	-----	-----	3477 br

w = Weak; m = medium; s = strong; vs = very strong; br = broad; sh = sharp.

1377 $\text{cm}^{-1}$  as a single sharp band in all the complexes. The band in the region 3302  $\text{cm}^{-1}$  due to symmetrical and asymmetrical stretching modes of  $\text{NH}_2$  in the spectra of 2-aph undergoes appreciable change in the spectra of the complexes in the range 3154 – 3253  $\text{cm}^{-1}$ . This shift to lower frequencies is a consequence of the coordination of the metal ion to the deprotonated amino group. The  $\nu(\text{M}-\text{N})$  is observed at 502 – 535  $\text{cm}^{-1}$ . This occurrence indicates that there is coordination between the metal and the lone pairs of electrons on the nitrogen atom of  $\text{H}_2\text{dmg}$ ,  $\text{dea}$  and  $2\text{aph}$ .

The  $\nu(\text{COO})$  and  $\nu(\text{CO})$  bands in the ligands were shifted to lower wave numbers and higher wave numbers respectively in all the complexes containing MOH as secondary ligand.

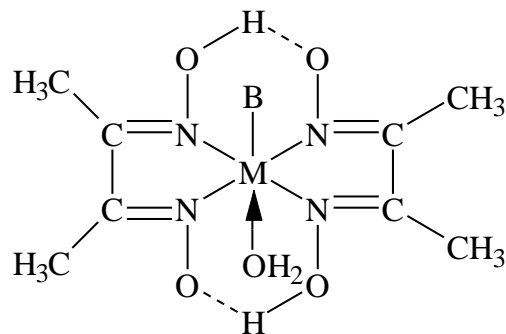
However, some new bands were observed in the region 620 – 723  $\text{cm}^{-1}$ . This indicates the formation of M-O bond for complexes containing 2-aph and MOH (Hamrit et al., 2000). This supports the coordination mode of ligand to the central metal ions via the oxygen atom of the carboxylate groups. However, such coordination was suggested to be covalent in nature (Nakamoto, 1986).

### Electronic spectra

The solution spectra of the complexes were done in DMSO and presented in Table 5. The UV/VIS spectra have been interpreted in terms of charge transfer transitions from metal to the  $\pi$  – antibonding orbital of the ligand based on literature (Cotton and Wilkinson, 1986). The absorption bands of the free ligands are due to transitions  $n - d^*$  and  $\pi \rightarrow \pi^*$  of the major chromophores present within the molecules. The transition metal ion  $\text{Co(II)}$  has a  $d^7$  electronic configuration, therefore has a spectroscopic ground state term symbol  $^4\text{F}$  and  $^4\text{P}$ . The  $^4\text{F}$  term is split into three sub energy levels namely  $^4\text{A}_{2g}$ ,  $^4\text{T}_{2g}$  and  $^4\text{T}_{1g}$ . The states  $^4\text{A}_{2g}$  (F) and  $^4\text{T}_{1g}$  (P) are very close. In irregular octahedral complexes these bands are likely to split and the extent of separation depends upon the amount of distortion present. In the present case, the assignments are not straight forward partly because of the poor resolution of the bands. The lowest energy band in the vicinity of 10,000  $\text{cm}^{-1}$  was seen due to the range of wavelength used. The bands at 17,860 and 21,230  $\text{cm}^{-1}$  have been assigned to  $^4\text{T}_1 \rightarrow ^4\text{A}_{2g}$  ( $^4\text{F}$ ) and  $^4\text{T}_{1g}$  ( $^4\text{P}$ ) respectively.

The electronic spectra of the  $\text{Cu(II)}$  complexes manifests charge-transfer band around 33,000  $\text{cm}^{-1}$  except  $[\text{Cu}(\text{Hdmg})_2(\text{MO})]$  which show a broad asymmetric ligand field band at 14,580  $\text{cm}^{-1}$  corresponding to  $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$  transition in a nearly octahedral arrangements.

The spectra of  $\text{Ni(II)}$  dimethylglyoximate complexes yielded three d-d transition in the regions 14,286, 17,391 and 27,855 - 31,056  $\text{cm}^{-1}$  assigned to the transition  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$  ( $^3\text{F}$ )( $\text{V}_1$ ),  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$  ( $^3\text{F}$ )( $\text{V}_2$ ) and  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$  ( $^3\text{P}$ )( $\text{V}_3$ ) transitions respectively.



**Figure 2.** Suggested structure of the complexes. B = 2aph, dea or MOH; M =  $\text{Co(II)}$ ,  $\text{Ni(II)}$  or  $\text{Cu(II)}$ .

The position and assignments for these bands indicates octahedral environment around the  $\text{Ni(II)}$  ion in these complexes (Aggarwal et al., 1981; Cotton and Wilkinson, 1986; Hamrit et al., 2000). Based on the IR and the UV/VIS spectrum, a tentative structure for the complexes may be assigned as in Figure 2.

### In vitro studies

The antibacterial and antifungal activities are presented in Tables 3 and 4, respectively. The results did show that, at low concentration of 1 mg/ml there was no activity against the two bacteria by both the ligands and the compounds. Whereas at 10 mg/ml, only malonic acid and diethylamine exhibits bacteriostatic activity against *E. coli* among the ligands.

In general, complexes of the  $\text{Co(II)}$  shows the highest inhibitory activity against *S. aureus* and *E. coli*. This is followed by the  $\text{Ni(II)}$  and  $\text{Cu(II)}$  complexes in that order. This confirms earlier reports. It was observed that, the susceptibility of the bacteria to the compounds was patterned after those compounds that contain the ligands in addition to dimethylglyoxime. The complexes exhibit a higher activity than the corresponding ligands. This confirms earlier reports (Nadira et al., 1987; Khadikar et al., 1994). However, *S. aureus* was more susceptible to the complexes than *E. coli*.

The antifungal activity of the ligands and the complexes examined showed different patterns. All the ligands prevented the growth of the fungi at a concentration of 10 mg/ml but less significant at 1 mg/ml.  $\text{Ni(II)}$  complexes showed 100% growth inhibition against *A. flavus*. This was followed by  $\text{Co(II)}$  and  $\text{Cu(II)}$  complexes, respectively, with  $[\text{Co}(\text{Hdmg})_2]$  showing the least activity of 37.5% (Yeamin et al., 2003).

It was observed that, all the complexes that showed activity of less than 75% causes the fungi to mutate. In general, *A. flavus* was more susceptible to all the complexes of 10 mg/ml. The complexation of the metal (II) ion with the ligand could be responsible for the fungi mutation

**Table 3.** Antibacterial activity of the ligands and the complexes on *E. coli* and *S. aureus*.

Compound	Concentration				Controls DMSO
	1 mg/ml		10 mg/ml		
	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	
Dimethylglyoxmine	00(100)	00(100)	00(100)	00(100)	00(100)
2 -aminophenol	01(99)	01(99)	02(98)	02(98)	00
Diethylamine	01(99)	00(100)	02(98)	08(98)	00
Malonic acid	01(99)	00(100)	02(98)	08(99)	00
[Co(Hdmg) <sub>2</sub> ]	00(100)	00(100)	00(100)	02(98)	00
[Co(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	00(100)	00(100)	10(88)	10(88)	00
[Co(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	00(100)	02(98)	08(90)	08(90)	00
[Co(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	00(100)	00(100)	01(99)	09(89)	00
[Ni(Hdmg) <sub>2</sub> ]	00(100)	00(100)	02(98)	02(98)	00
[Ni(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	00(100)	00(100)	04(95)	04(95)	00
[Ni(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	00(100)	00(100)	08(90)	08(90)	00
[Ni(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	00(100)	00(100)	10(88)	02(98)	00
[Cu(Hdmg) <sub>2</sub> ]	00(100)	00(100)	07(97)	02(98)	00
[Cu(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	00(100)	00(100)	09(89)	06(93)	00
[Cu(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	00(100)	00(100)	03(96)	00(100)	00
[Cu(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	00(100)	00(100)	09(89)	10(88)	00

Figures represent zones of inhibition (in mm) after 24 - 48 h; values in brackets indicate % diameter of inactive.

**Table 4.** Antifungal activity of the ligands and the complexes on *A. flavus* and *A. niger*.

Compound	Concentration				Control	
	1 mg/ml		10 mg/ml		DMSO	PDA
	<i>A. niger</i>	<i>A. flavus</i>	<i>A. niger</i>	<i>A. flavus</i>		
Dimethylglyoxmine	10 (120)	12 (24)	100 (0)	100 (0)	000 (NM)	000 (NM)
2 -aminophenol	-----	10 (24)	100 (0)	100 (0)	"	"
Diethylamine	-----	13 (20)	100 (0)	100 (0)	"	"
Malonic acid	-----	10 (80)	100 (0)	100 (0)	"	"
[Co(Hdmg) <sub>2</sub> ]	10 (160)	-----	75 (5)	37.5 (35)	"	"
[Co(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	10 (100)	15 (40)	75 (12)	100 (0)	"	"
[Co(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	-----	-----	62.5 (16)	50 (84)	"	"
[Co(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	-----	12.5 (32)	50 (104)	100 (0)	"	"
[Ni(Hdmg) <sub>2</sub> ]	12.5 (120)	18.7 (20)	75 (12)	100 (0)	"	"
[Ni(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	-----	10 (28)	62.5 (12)	100 (0)	"	"
[Ni(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	12.5 (120)	10 (180)	100 (0)	100 (0)	"	"
[Ni(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	15 (00)	-----	100 (0)	62.5 (4)	"	"
[Cu(Hdmg) <sub>2</sub> ]	-----	-----	37.5 (396)	50 (4)	"	"
[Cu(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	-----	20 (28)	50 (304)	100 (0)	"	"
[Cu(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	10 (16)	-----	75 (104)	50 (20)	"	"
[Cu(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	-----	13 (80)	62.5 (360)	100 (0)	"	"

Figures represent the % inhibition of fungal growth after 3 days (72 h) and those in bracket are the average colony numbers; -- % inhibition less than 10; NM = numerous.

which is more pronounced with the Cu(II) complexes.

## Conclusion

All the complexes are air-stable and generally insoluble in

most common non-coordination organic solvents. Based on their electronic spectral results an octahedral geometry is suggested for the complexes. Microanalysis and magnetic moment measurements could not however, be carried out on the complexes due to instrument limitation in order to further confirm the geometries. The *in vitro* anti-

**Table 5.** Electronic spectral bands of the complexes.

Compound	Band Positions (kK), 1 kK= 1000cm <sup>-1</sup>			
	Band I	Band II	Band III	Band IV
2 -aph	32.79			
Dea	46.08			
MOH	32.68			
H <sub>2</sub> dmg	46.38	30.67		
[Co(Hdmg) <sub>2</sub> ]	33.67			
[Co(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	45.46	31.47		
[Co(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	32.05	21.23	17.86	
[Co(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]			17.87	
[Ni(Hdmg) <sub>2</sub> ]	32.05			
[Ni(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]		27.86	14.29	
		31.06		
		26.46		
[Ni(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]		30.67	17.39	
[Ni(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]		29.07		
[Cu(Hdmg) <sub>2</sub> ]	45.46	31.65		
[Cu(Hdmg) <sub>2</sub> (2aph)(H <sub>2</sub> O)]	33.56	23.81		
[Cu(Hdmg) <sub>2</sub> (dea) <sub>2</sub> ]	32.90			
[Cu(Hdmg) <sub>2</sub> (MO)(H <sub>2</sub> O)]	32.79		14.58	

microbial screening on the complexes showed that they are potential antibacterial and antifungal agents against the tested microorganisms at 10 mg/ml.

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