

Synthesis, Physico-Chemical and Antimicrobial Properties of Co(II), Ni(II), and Cu(II) Mixed-Ligand Complexes of Dimethylglyoxime

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Abstract: The synthesis of non-electrolyte mixed-ligand complexes of the general formula $[M(\text{Hdmg})\text{B}]$, where $M = \text{Co(II)}, \text{Ni(II)}$ or Cu(II) $\text{Hdmg} = \text{dimethylglyoximato monoanion}$, $\text{B} = 2\text{-aminophenol(2-aph)}$, diethylamine (dea) or malonic acid (MOH) are described. Metal analysis, melting points, solubility, conductivity, IR and UV/Visible electronic spectra were used in determining their physico-chemical properties. The antimicrobial activities of the complexes were tested against *Esherichia 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 colours of the complexes are mostly dark - brown or red. The spectral results suggest the binding of Hdmg, 2-amino phenol or malonic acid through the N atom and O atoms respectively to the metal ion. In the electronic spectra of the complexes, the absorption bands observed in the UV/Visible 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 marked antimicrobial activity against the tested microbes at 10 mg/mL. The possible use of the complexes as chemotherapeutic agents is hereby suggested.

Key words: Antimicrobial activity, dimethylglyoxime, infrared spectroscopy, mixed - ligand, UV/Visible spectroscopy

INTRODUCTION

In the last few years, there has been a great surge in the development of chelation chemistry and its use in medicine and related areas of life science research (Robert, 1994). As a result metal complexes have been gaining increasing importance in the design of respiratory, slow release and controlled release drugs. Equally, the efficacies of some therapeutic agents are known to increase upon coordination (Ajibola, 1990; Obaleye *et al.*, 1997). Some metal complexes, especially mixed-ligand complexes, are known to exhibit remarkable activities (Kudirat *et al.*, 1994; Yeamin *et al.*, 2003; Oguniran *et al.*, 2007).

As part of our interest in the preparation of mixed-ligand complexes, we have previously reported the synthesis, physico-chemical and antimicrobial properties of some mixed-ligand complexes of the general formula $(\text{M}(\text{Hdmg})_2\text{B})$, where $\text{Hdmg} = \text{dimethylglyoximato monoanion}$ $\text{B} = \text{aminophenol}$, diethylamine or malonic acid (Osunlaja *et al.*, 2009). As a continuation of our work on similar complexes, we have now extended this to a new series containing only one Hdmg with the same sets of secondary ligands. The synthesis, physico-chemical and antimicrobial properties for these complexes are detailed in this study.

MATERIALS AND METHODS

All chemical reagents and solvents used were of analytical grade and were used without further purification. The complexes were prepared according to modifications of literature procedures (Schrauzer, 1968; Kolawole and Ndahi, 2004). The metals were analyzed by complexometric methods (Vogel, 1978). The infrared spectra were recorded on a Genesis II FTIR spectrophotometer in the range 4000-450 per cm (as KBr discs) at the Advance laboratory, Sheda Science and Technology Complex (SHESTCO), Sheda Abuja, Nigeria. The electronic absorption spectra of 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, Nigeria.

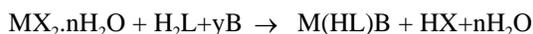
The conductivity measurements were performed at room temperature (33°C) using an electrolytic conductivity set, Crison Conductimeter 522, with a cell constant of 1.52 on the complexes that were soluble in either methanol or DMSO at a concentration of 10^{-3} mold m^{-3} . A Griffin melting point apparatus was used to measure the melting points/ decomposition temperatures (M.P./D.T.).

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 making a solution of the ligand, Hdmg (3 mmol, 0.34835 g) in 80 mL boiling EtOH with 3 mmol, (0.8731, 0.7465 and 0.5980 g) of the appropriate metal(II) salt dissolved in 20 mL of distilled water. The mixture was magnetically stirred for about 1hr after which 3mmol of the secondary ligands: 0.3274 g (2-aminophenol), 0.3122 g (malonic acid) previously dissolved in 20 mL of EtOH was added with magnetic stirring to each preparation. This was refluxed for another 1 h. For diethylamine, 6 mmol (0.62 mL) were used.

The precipitates were filtered and washed with 3x5 mL portions of 50% ethanol/water mixture and then with 2x5 mL portions of ethanol. The products were dried in a desiccator over CaCl₂.

The general equation for the synthesis is as follows:



where, M = Co(II), Ni(II) or Cu(II); X = NO₃⁻, 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 ligands and the complexes were determined by a previously described method (Robert and

Allen, 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). The bacterial and fungal cultures were incubated at 37°C for 48 and 72 h respectively. The antibacterial and antifungal activities interpretations are as reported in our earlier work (Osunlaja *et al.*, 2009).

RESULTS AND DISCUSSION

The suggested molecular formula/molar mass, colour, melting points/decomposition temperatures, %yield, %metal and conductivity of the complexes are given in Table 1. The complexes exhibit various shades of colour: those of Co(II) were brown of different intensities; Ni(II) complexes were red and those of Cu(II) were dark brown, black and dark green. The melting points falls within range 120-306°C with those of Ni(II) being the highest. [Ni(Hdmg)(2aph)] and [Cu(Hdmg)dea, however decomposed before melting. The % yield corresponds roughly to the mole ratio of the metal: ligand used in comparison with those complexes containing 2 mol of Hdmg as we had earlier reported (Osunlaja *et al.*, 2009).

All the complexes have varying degree of solubility in the organic solvents used and, except for the Co(II) complexes, the complexes were insoluble. This is suggestive of the fact that the complexes are non- polar. The molar conductance values of the complexes (0.06-

Table 1: Some physical properties of the mixed-ligand complexes

Compound	Molecular formulae (Molar mass)	Colour	M.P/D.T. (°C)	Yield %	mol	$\Delta_m/\Omega/cm^2/$ % M found (Calcd)
[Co(Hdmg)(2aph)]	CoC ₁₀ H ₁₄ N ₃ O ₃ (283.18)	Brown	120	63.1	0.100	20.70(20.8)
[Co(Hdmg)(dea) ₂]	CoC ₁₂ H ₂₉ N ₂ O ₂ (320.33)	Dark Brown	290	40.8	0.100	18.32(18.40)
[Co(Hdmg)(MO)]	CoC ₇ H ₆ N ₂ O ₆ (276.11)	Golden Brown	244	73.4	0.181	21.50(21.34)
[Ni(Hdmg)(2aph)]	NiC ₁₀ H ₁₄ N ₃ O ₄ (282.94)	Dark Rose Red	305-306 (d)	49.8	0.106	20.60(20.70)
[Ni(Hdmg)(dea) ₂]	NiC ₁₂ H ₂₉ N ₂ O ₄ (320.08)	Red	304	47.5	0.094	18.24(18.34)
[Ni(Hdmg)(MO)]	NiC ₇ H ₆ N ₂ O ₆ (275.87)	Brownish Red	306	70.4	0.100	21.41(21.27)
[Cu(Hdmg)(2aph)]	CuC ₁₀ H ₁₄ N ₃ O ₃ (287.80)	Dark Brown	204	47.70	0.069	22.33(22.08)
[Cu(Hdmg)(dea) ₂]	CuC ₁₂ H ₂₉ N ₂ O ₂ (324.94)	Black	240 (d)	34.57	0.062	19.75(19.56)
[Cu(Hdmg)(MO)]	CuC ₇ H ₆ N ₂ O ₆ (280.73)	Dark-green	206	76.87	0.071	22.32(22.64)

d: Decomposition temperature; M: Co(II), Ni(II), or Cu(II)

Table 2: Relevant infrared frequencies (per cm) for the ligands and their complexes

Compound	V(C=N)	V(N-O)	V(N'-O)	V(M-N)	V(M'-N)	V(M-O)	V(COO')	V(C-O)	V(NH)	V(NH ₂)	V(O-H)
2-aph	1377s 1281m	-	-	-	-	-	-	1216 sh	-	3304sh 3374sh	3490 sh
Dea	1385 sh	-	-	-	-	-	-	-	3102 w	-	-
MOH	-	-	-	-	-	-	1680	b1307	-	-	2942 br
H ₂ dmg	1454vs	1142 s	977vs 902vs	-	-	-	-	-	-	-	3228 br
[Co(Hdmg)(2aph)]	1462s	1154 w	1083 m	507 w	-	722 s	-	-	-	3154 m	3381 br
[Co(Hdmg)(dea) ₂]	1462vs	1206 s	1082 s	510 s	410 s	-	-	-	3174 w	-	3430 br
[Co(Hdmg)(MO)]	1454m	1235 m	1080 m	510 w	-	668 w	1591 m	1336 m	-	-	3403 br
[Ni(Hdmg)(2aph)]	1461vs	1240 s	1100 s	520 s	-	722 s	-	-	-	3189 w	3415 br
[Ni(Hdmg)(dea) ₂]	1462vs	1239 s	1100 s	520 s	-	-	3224 w	-	-	-	3446 br
[Ni(Hdmg)(MO)]	1461s	1239 s	1100 s	520 s	-	722 s	1572 s	1377s	-	-	3443 br
[Cu(Hdmg)(2aph)]	1461v	1298 s	1100 s	522 s	499 s	620 s	-	-	-	3253 m	3451 br
[Cu(Hdmg)(dea) ₂]	1462vs	1197 m	1078 m	520 w	498 s	-	-	3245 w	-	-	3399 br
[Cu(Hdmg)(MO)]	1461s	1232 m	1089 m	510 w	-	722 s	1612 m	1377s	-	-	3428 br

w: weak; m: medium; s: strong; vs: very strong; br: broad; sh: shoulder

Table 3: Electronic spectra bands of the ligands and their complexes

Compound	Band positions (kK), 1 kK = 1000 / cm			
	Band I	Band II	Band III	Band IV
2-aph	32.79			
	46.08			
Dea	32.68			
MOH	46.38	30.67		
H ₂ dmg	33.67			
[Co(Hdmg)(2aph)]	31.54	21.23	19.76	
[Co(Hdmg)(dea) ₂]		26.33		
[Co(Hdmg)(MO)]	31.75			
[Ni(Hdmg)(2aph)]		30.67	17.58	
[Ni(Hdmg)(dea) ₂]		30.67	17.58	
[Ni(Hdmg)(MO)]		31.05		
[Cu(Hdmg)(2aph)]	46.08	23.31		
		30.49		
CuHdmg)(dea) ₂	32.36			
[Cu(Hdmg)(MO)]	46.08			
	32.79			

0.18 Ω^{-1} cm² mol⁻¹) revealed that the complexes are non-electrolytes.

The metal analysis of the complexes is consistent with the calculated values from the empirical formula of each compound. Thus, based on the analytical data in Table 1, the general formula of the complexes may be proposed as [M(Hdmg)(B)], where M = Co(II), Ni(II) or Cu(II); B = 2 aph, dea or MOH. That is to assume that the dimethylglyoximate group acts as monoanion (Adkhis *et al.*, 2000). The secondary ligands MOH and 2aph were bidentate while dea was monodentate.

Spectral properties of the complexes:

Infrared: The tentative assignments of the bands (Table 2) are made based on reports of similar studies of dimethylglyoximate complexes and/or on related compounds and also by comparing the spectra of the complexes with the spectra of the ligands.

The $\nu(\text{C}=\text{N})$ frequency at 1454 per cm in free H₂dmg is observed at around 1461-1464 per cm in the spectra of the complexes. This suggests that the ligand is coordinated to the metal ions through the nitrogen of the oxime (Adkhis *et al.*, 2003). The appearance of a single strong band at 1454 per cm in H₂dmg shows that the two oxime groups are identical while the appearance of a band for the complexes at around 1142-1298 per cm, is assignable to $\nu(\text{NO})$. In all the complexes, $\nu(\text{O}-\text{H})$ band is observed at 3381-3345 per cm which is at higher wave numbers compared with those of the ligands. In our earlier work, these shifts were attributed to O--H-O hydrogen bridges between the dimethylglyoximate ions (Nakamoto, 1986). However, in this case, the $\nu(\text{O}-\text{H})$ band may not have been a result of hydrogen bridges, but, rather of unbound OH group since the complexes contains only one mole of H₂dmg.

The $\nu(\text{NH})$ bands of the complexes containing dea undergo a hypsochromic shift in comparison with the ligand. On the other hand, a bathochromic shift was observed for $\nu(\text{NH}_2)$ band of the complexes containing 2aph. These shifts are in agreement with earlier reports

and a result of the coordination to the metal through the N atoms of these ligands (Nakamoto, 1986). The $\nu(\text{M}-\text{N})$ bands were observed at 507-522 per cm.

The asymmetric and symmetric stretching vibrations of the carboxylate groups ($\nu(\text{COO}^-)$) of malonic acid (MOH) were observed at about 1680 per cm as a band. This band was shifted to a lower wave number in the complexes. This shift agrees with earlier reports and is an indication of chelation of the ligand through the carboxylate groups to the metal ions (Udupa and Ramachandra, 1981; Gloria *et al.*, 2005). Thus the bands observed at 620-722 per cm were assigned to $\nu(\text{M}-\text{O})$ in complexes containing 2aph and MOH. These indicates that the O atom of 2aph (from-OH group) and those of MOH (from -COOH group) were coordinated to the metal ion.

Electronic spectra: The UV/Visible spectrum (Table 3) of free 2aph, dea, MOH and H₂dmg showed major absorption bands around Band I. These bands are probably due to intra-ligand or charge transfer transitions. The spectra of [(Co(Hdmg)(2aph)] showed well resolved absorption bands in I, II and III and have been assigned to metal to ligand charge transfer (MLCT), $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$, and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}(\text{P})$, respectively in a nearly tetrahedral environment. [Co(Hdmg)(dea)₂] gave a band of medium intensity of 26,300 per cm in II and was assigned to $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$ in a nearly tetrahedral environment. The complex containing MO showed an absorption band around 32,000 per cm and is assigned to MLCT. The above assignments agree with the literature (Cotton *et al.*, 2004). Furthermore in accordance with earlier reports, tetrahedral Co(II) complexes should show bands in a lower frequency region, i.e., around 10,000 per cm, associated with the transition $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$ (Cotton and Wilkinson, 1986), which according to Cotton and Wilkinson is seldom observed because it is an inconvenient region of the spectrum and because it is orbitally forbidden (Sharma *et al.*, 1981).

The spectra of Ni(II) complexes except [Ni(Hdmg)(MO)] showed two d-d transitions which have been assigned to $^3\text{T}_{1g}(\text{F})^3 \rightarrow ^3\text{A}_{2g}$ and $^3\text{T}_{2g}(\text{F})^3 \rightarrow ^3\text{A}_{2g}$ respectively. The positions and assignments of these bands indicated a nearly tetrahedral environment around the Ni(II) ion in these complexes. The above observations are in close agreement with previous assignments. This is with the understanding that transition from the $^3\text{T}_1(\text{P})$ ground state in a tetrahedral symmetry to the $^3\text{T}_1(\text{F})$ state occurs in the visible region and is relatively strong compared to the corresponding $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ transition in octahedral complexes (Sharma *et al.*, 1981).

From literature crystal field theory predicts one transition $^2\text{T}_{2g} \rightarrow ^2\text{E}_g$ for truly tetrahedral copper (II)

Table 4: Antibacterial activity of the ligands and their complexes against *E.coli* and *S.aureus*

Compound S.A.	Concentration Controls				
	1 mg/mL		10 mg/mL		Control DMSO
	S.A.	E.C.	S.A.	E.C.	
Dimethylglyoximine	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(90)	00
Malonic Acid	01(99)	00(100)	02(98)	08(90)	00
[Co(Hdmg)(2aph)]	00(100)	02(98)	08(90)	08(90)	00
[Co(Hdmg)(dea) ₂]	00(100)	00(100)	08(90)	06(93)	00
[Co(Hdmg)(MO)]	01(99)	02(98)	00(100)	04(95)	00
[Ni(Hdmg)(2aph)]	00(100)	00(100)	09(89)	08(90)	00
[NiHdmg)(dea) ₂]	00(100)	00(100)	13(84)	06(93)	00
[Ni(Hdmg)(MO)]	00(100)	00(100)	04(95)	00(100)	00
[Cu(Hdmg)(2aph)]	00(100)	00(100)	10(88)	00(100)	00
[Cu(Hdmg)(dea) ₂]	00(100)	00(100)	05(94)	00(100)	00
[Cu(Hdmg)(MO)]	00(100)	00(100)	06(93)	00(100)	00

Figures represent zones of inhibition (in mm) after 24 - 48 hours; S.A.: *Staphylococcus aureus*; E.C.: *Escherichia coli*; DMSO: Dimethylsulphoxide

Table 5: Antifungal activity of the ligands and their complexes against *A. flavus* and *A. niger*

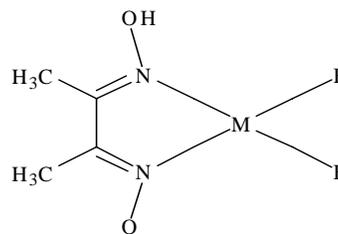
Compound	Concentration					
	1 mg/mL		10 mg/mL		Control	
	A.N.	A.F.	A.N.	A.F.	DMSO	PDA
Dimethylglyoximine	10(120)	12(24)	100(0)	100(0)	000 (NM)	000 (NM)
2-Aminophenol	-	10(24)	100(0)	100(0)	00	00
Diethylamine	-	13(20)	100(0)	100 (0)	00	00
Malonic Acid	-	10(80)	100(0)	100(0)	00	00
[Co(Hdmg)(2aph)]	-	13(32)	50(312)	100 (0)	00	00
[Co(Hdmg)(dea) ₂]	10(216)	12.5(80)	7.5 (44)	100(0)	00	00
[Co(Hdmg)(MO)]	-	5(20)	50(164)	75(240)	00	00
[Ni(Hdmg)(2aph)]	-	18.7(24)	50(364)	100(0)	00	00
[NiHdmg)(dea) ₂]	10(100)	13(40)	75(12)	100(0)	00	00
[Ni(Hdmg)(MO)]	13(200)	18.7(44)	100(0)	100(0)	00	00
[Cu(Hdmg)(2aph)]	-	-	62.5(116)	50(20)	00	00
[Cu(Hdmg)(dea) ₂]	-	-	50(344)	50(24)	00	00
[Cu(Hdmg)(MO)]	-	18.7(20)	62.5(208)	100(0)	00	00

Figures represent the % inhibition of fungal growth after 3 days (72 h) and those in brackets are the average colony numbers; -: % inhibition less than 10

complexes (Rajendra *et al.*, 1981). In the present study all absorption bands were located in Band I except [(Cu(Hdmg)(2aph)] that shows two other bands in II. These absorption bands are presumably assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ in a pseudo-tetrahedral configuration and those present in I are assigned to MLCT. Based on the FT-IR and the UV/Visible spectrum, a tentative structure for the complexes may be assigned as in Fig. 1.

Antimicrobial activities: The antibacterial and antifungal activities of the ligands and the complexes are presented in Tables 4 and 5, respectively. In general, complexes of Co(II) shows the highest inhibitory activity against the two bacteria isolates. This is followed by Ni(II) and Cu(II) complexes in that order. The latter only been effective against *Staphylococcus aureus*. In all, [(Ni(Hdmg)(dea)₂] exerts the highest inhibitory activity against *Staphylococcus aureus* at ≥ 13 mm.

Also, both the ligands and the complexes show no tangible activity against the two bacteria at a low



B = 2-aph, dea or MOH, M = Co(II), Ni(II) or Cu(III)

Fig. 1: Suggested structure of the complexes

concentration of 1 mg/mL. That is to postulate that, the inhibitory activity of the complexes will increase as the concentration increases and the activity of the ligands against the isolates increases upon chelation. In comparison to our earlier work, *Staphylococcus aureus* was more susceptible to the complexes than *Escherichia coli*.

From the result of the antifungal activity, the complexes of Ni(II) showed 100% growth inhibition against *Aspergillus flavus*. This is followed by the Co(II) and Cu(II) complexes respectively. This confirms earlier reports (Kudirat et al., 1994). It was also observed that, all the complexes that showed activity of less than 75% caused the fungi to mutate (Hawker and Linton, 1979). The complexation of the metal (II) ion with the ligand could be responsible for the mutation as a result of the fungi's cell wall adaptation to the chemical effects of the complexes, which is more pronounced with the Cu(II) complexes. In general, *Aspergillus flavus* was more susceptible to all the complexes at 10 mg/mL. The present results of the *in vitro* studies are similar to those for the complexes containing 2 moles of H₂dmg. Hence, it seems safe to say that the number of moles of H₂dmg used have not significantly affected the antimicrobial activities of the complexes. containing 2 moles of H₂dmg. Hence, it Thus, this supports previous investigations of coordination complexes (Hamida, 1994; Islam *et al.*, 2002; Saidu *et al.*, 2003).

CONCLUSION

The compounds are mostly brown or red in colour and are characterized by high melting points/decomposition temperature. All the complexes are air-stable and generally insoluble in most common non-coordinating solvents. Results from the conductivity measurements indicate that they are non-electrolytes. The coordination in the complexes occurs through the N of oxime, dea, amino group of 2-aph and also through the O of the -COOH and -OH groups of MOH and 2-aph respectively. This is supported by the increase of the $\nu(C=N)$ frequencies in the FT-IR spectra of most of the complexes compared to the ligand and the observed increase in $\nu(N-O)$ stretching mode.

The UV/Visible solution spectrum suggests a distorted tetrahedral geometry which could not however be further confirmed with microanalysis and magnetic moment measurements due to instrument limitation.

The *in vitro* antimicrobial screening of the complexes showed that they are potential chemotherapeutic agents against the tested micro organisms at 10 mg/mL.

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