https://dx.doi.org/10.4314/ijs.v19i1.12

SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL STUDIES OF MIXED NICKEL(II) AND COPPER(II) COMPLEXES OF AROYLHYDRAZONES WITH 2, 2^1-BIPYRIDINE AND 1, 10-PHENANTHROLINE

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(Received: April, 2017; Accepted: July, 2017)

ABSTRACT

Herein, we report the synthesis of 2-anisaldehyde-benzoylhydrazone (L_1), vanillin-benzoylhydrazone (L_2**)** and mixed Ni(II) and Cu(II) complexes of L_1 and L_2 with 2, 2^1-bipyridine and 1, 10-phenanthroline (N-N bases). The resulting compounds were characterized by ^{1}H NMR, IR, UV-VIS, Solubility studies, percentage Metal analysis, Conductivity measurements, and Magnetic Moment measurements. ^{1}H NMR spectra indicated the formation of the ligands. IR Spectra showed that the ligands coordinated in enol form through the deprotonated carbonyl bond (C=O) and the azomethine (C=N). The (N-N) bases similarly coordinated through the (C=N). The magnetic moment values for the Cu(II) complexes ranges from 2.14 to 2.36 B.M Magnetic moment values ranging from 2.78 to 3.11 B.M were found for the complexes of Nickel except [Ni(L_2)(bpy)]Cl and [Ni(L_2)phen]Cl that had moment of 0.49 and 0.75 B.M respectively. Conductance values indicated a 1:1 electrolyte for the complexes. The antimicrobial activities of the ligands and their mixed ligand complexes were screened using Agar diffusion method. It was found that the mixed metal complexes have higher antimicrobial activity than the free ligands.

Keywords: Benzylhydrazone, Spectroscopy, Magnetic moment, Geometry, Zone of inhibition.

INTRODUCTION

Hydrazones are a class of organic compounds that are characterized with the presence of $R_1R_2C{=}N{-}NH{-}$ atomic linkage. They are formed by the condensation of hydrazides or hydrazide derivatives with aldehydes or ketones (Deepa and Aravindakshan, 2005). They contain two connected nitrogen atoms of different nature and an azomethine (C=N) that is conjugated with a lone pair of electrons of the terminal nitrogen atom (Walcourt *et al*., 2004). These structural fragments are mainly responsible for the physical and chemical properties of the compounds. The two nitrogen atoms of these groups of compounds are nucleophilic, although, the amino nitrogen is more reactive. The carbon atoms of hydrazone group are both electrophilic and nucleophilic in character hence; they are widely used in organic synthesis, especially for the preparation of heterocyclic compounds. The ease of preparation, increased hydrolytic stability relative to imines, and tendency toward crystallinity are characteristics that make hydrazones desirable (Wang *et al*., 2013).

Hydrazones have interesting biological properties, which include anti-inflammatory and antimalarial (Fattorusso *et al*., 2008), analgesic, anticonvulsant, antituberculous, antitumor (Al-Said *et al*., 2011), anti-HIV and antimicrobial activities, hence they constitute an important class of compounds for new drug development (Rollas and Kucukguzel, 2007; Gokce *et al*., 2009; Ahmed *et al.,* 2014). There are several reports on the synthesis, structural characterization and biological activities of transition metal complexes containing different types of hydrazone ligands (Shen and Jiang, 1995; Galal *et al.,* 2009; Hosny *et al.,* 2010; Agwapa *et al.,* 2010;). Mixed chelates of Aroylhydrazones with base ligand such as 1,10-phenanthroline, 2, 2^1-bipyridine (Niu *et al*., 2007) and 2-amino-4-methylpyridine (Sreeja *et al*., 2004) have been reported and found to exhibit enhanced antimicrobial properties than the metal(II) complexes. However, report on synthesis, physicochemical studies and anti-microbial activity of mixed Ni(II) and Cu(II) complexes of 2-anisaldehyde-benzoylhydrazone (L_1), vanillin-benzoylhydrazone (L_2**)** with 2, 2^1-bipyridine and 1, 10-phenanthroline are scanty. The results of this study are herein reported.

EXPERIMENTAL

Reagents and solvents

All the chemicals and solvents employed were of BDH and Sigma Aldrich quality and used without further purification. They are Ethylbenzoate, Vanillin (3-methoxy-4-hydroxyl-benzaldehyde), 2-Anisaldehyde (2-methoxy-benzaldehyde), ethylenediaaminetetraacetic acid (disodium salt), Dimethylsulphoxide (DMSO), Dimethylformamide (DMF), Acetone, Diethylether, Methanol, Ethanol, Hydrazine hydrate. Copper (II) chloride dihydrate and Nickel(II) chloride hexahydrate. The metal contents (w/w %) were determined by complexometric titration of EDTA using murexide indicator and ammonia/ammonium chloride buffer. IR Spectra were recorded in the range 4000-400 cm^{-1} using KBr discs on Shimadzu FT-IR 8000 Spectrometer at Redeemer's University, Ede, Osun State. UV-Vis spectra of the samples were measured in the range 1000 – 200 cm^{-1} using a Shimadzu UV-Vis 1800 Spectrophotometer at Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria. The magnetic susceptibility of the samples was measured with a Sherwood Scientific Magnetic susceptibility balance, MSB Mark1 at University of Ibadan, Nigeria. Melting Points of the compounds were determined using a Gallenkamp melting point Apparatus at Obafemi Awolowo University, Ile-Ife, Nigeria.

Synthesis of Hydrazone

The preparation of the Hydrazone was done in two steps: the first step involved the preparation of the Benzoyl hydrazide, while the second step yielded the Hydrazones.

Preparation of Hydrazide

Ethylbenzoate (63 ml, 400 mmol) in 70 ml ethanol and hydrazine hydrate (19.40 ml, 400 mmol) in 15 ml of ethanol were mixed in a 250 ml round bottom flask and the mixture was heated under reflux for 12 hours. The resultant yellow solution was concentrated using rotary evaporator to obtain a white crystalline precipitate which was washed several times with 40% ethanol to obtain white crystalline solid. It was dried in the desiccator over $CaCl_2$. M.pt. 110-112 °C

Synthesis of Hydrazone [VBH (L_2)]

Benzoylhydrazide (0.3 g, 0.22 mmol.) in 20 ml of absolute ethanol was added dropwise into 20 ml of ethanolic solution of 4-hydroxy-3-methoxybenzaldehyde (3.35 g, 0.22 mmol). The mixture was stirred and refluxed for 4 hours. The mixture was left overnight in a beaker to form precipitate after which the white crystalline precipitate was filtered and washed with 40% ethanol and dried in a desiccator over $CaCl_2$. The same method was used for L_1 (2-ABH).

Preparation of Metal(II) Hydrazone Mixed with 1,10-Phenanthroline

The ligands (L_1/L_2), (1.1 mmol) were dissolved in (10 ml) of 1:1 absolute ethanol/acetone mixture in a 100 ml beaker and allowed to stir for 10 minutes. Then, an ethanolic solution of metal(II)chlorides (1.1 mmol) and ethanolic solution of 1,10-phenanthroline (1.1 mmol) were simultaneously added dropwise to the stirring mixture. The mixtures were stirred for 6 hrs at room temperature after which the precipitate formed was filtered and washed using 40% ethanol and dried in a desiccator over calcium chloride.

$L_1/L_2 + MCl_2.xH_2O + phen \rightarrow [M(L_1/L_2)(phen)(H_2O)_2]Cl + HCl + xH_2O$

Synthesis of Metal(II) Hydrazone Mixed with 2,2-Bipyridine

The ligands, L_1/L_2 (1.1 mmol) were dissolved in a 1:1 ethanol/acetone mixture (10 ml) in a 100ml beaker and allowed to stir for 10 minutes after which an ethanolic solution of metal(II) chloride (1.1 mmol) and ethanolic solution of $2,2^1$-bipyridine (1.1 mmol) was added dropwise to the stirring mixture. The reaction mixture was stirred at room temperature for 2 to 6 hours after which the precipitate were filtered under suction, washed with 40% ethanol and dried in a desiccator over $CaCl_2$.

$L_1/L_2 + MCl_2.6H_20 + bipy \rightarrow [Ni(L_1/L_2)(bipy)]Cl + HCl + xH_2O$

RESULTS AND DISCUSSION

General comments.

Nickel(II) and Copper(II) complexes of aroylhydrazones mixed with $2,2^1$- bipyridine and

1,10- phenanthroline have been prepared according to method described in the literature (Patel and Woods, 1990; Wang *et al.,* 2008; Singh and Singh, 2012) and were characterized with a view of proposing their geometry and stoichiometry. Physicochemical properties of the compounds including colour, melting point/decomposition temperature and percentage yields, are presented in Table 1. The two ligands (L_1 and L_2) synthesized are white. The mixed ligand copper(II) complexes with $2,2^1$-bipyridine and 1,10-phenathroline are generally green while nickel(II) complexes mixed with $2,2^1$-bipyridine and 1,10-phenanthroline respectively display colours ranging from orange to deep green. The melting point of L_1 is 193-195°C and L_2 is 128-130°C. All the mixed metal(II) complexes of 2-ABH (L_1) have melting point in the range of 251-269°C while the mixed complexes of VBH (L_2) ranges from 269 to 285°C indicating high thermal stabilities for the complexes.

There was a fair agreement between the calculated %metal and the observed for the metal complexes. The results suggested a ratio 1:1:1 for metal to ligand to base. The compounds are fairly soluble in methanol, DMF and DMSO with varying degree of solubility in the eight common solvents. These physico-chemical parameters are shown in Table 1, while their solubilities are displayed in Table 2.

^{1}H-NMR

The ^{1}H-NMR in DMSO-d_6 of L_1 (Figure 1a, Appendix) shows multiplet signals in the range 6.91 to 7.90 ppm due to aromatic protons. The signal at 8.70 ppm (1H, s) is due to the azomethine proton (HC=N-). The signal at 10.50 ppm (1H, s) corresponds to the amide type N-H Proton. The signal at 3.90 ppm (3H, s) correspond to the methoxy group ($–OCH_3$) while the signal at 2.10 ppm is due to the solvent proton.

The ^{1}H-NMR of the L_2 in DMSO-d_6 (Figure 1b) shows multiplet signals in the range 6.86 to 7.90 ppm which corresponds to the aromatic protons. The signal at 3.84 ppm (3H, s) correspond to the proton of methoxy ($–OCH_3$) group while the amide type proton (N-H) appeared at 11.68 ppm. The signal at 8.30 ppm (1H, s) is due to the azomethine proton (HC=N-), while the signal at 2.50 ppm and 3.30 ppm are the solvent peaks.

Table 1: Physical properties and analytical data for the complexes

Complex	Formula (Formula weight (g/mol))	Colour	Melting point.(°C)	% Metal found (Calculated)	% Yield
2-ABH (L_1)	$C_{15}H_{14}N_2O_2$ (254.34)	White	193-195		88
$[Cu(L_1)(bpy)(H_2O)_2]Cl$	$C_{25}H_{26}N_4O_4ClCu$ (545.50)	Green	256-258	12.48 (12.71)	28
$[Cu(L_1)(phen)(H_2O)_2]Cl$	$C_{27}H_{26}N_4O_4ClCu$ (569.52)	Green	266-269	11.53 (12.10)	43
$[Ni(L_1)(bpy)(H_2O)_2]Cl$	$C_{25}H_{26}N_4O_4ClNi$ (540.64)	Deep green	251-253	12.00 (11.74)	22
$[Ni(L_1)(phen)(H_2O)_2]Cl$	$C_{27}H_{26}N_4O4ClNi$ (546.42)	Deep green	261-263	10.74 (11.00)	19
VBH (L_2)	$C_{15}H_{14}N_2O_3$ (270.28)	White	128-130		84
$[Cu(L_2)(bpy)(H_2O)_2]Cl$	$C_{25}H_{26}N_4O_5ClCu$ (561.50)	Green	282-285	12.09 (12.48)	48
$[Cu(L_2)(phen)(H_2O)_2]Cl$	$C_{27}H_{26}N_4O_5ClCu$ (585.52)	Green	275-278	11.19 (10.85)	41
$[Ni(L_2)(bpy)]Cl$	$C_{25}H_{22}N_4O_3ClNi$ (520.61)	Orange	277-279	11.30 (11.64)	28
$[Ni(L_2)(phen)]Cl$	$C_{27}H_{22}N_4O_3ClNi$ (544.63)	Orange	269-271	10.43 (10.61)	41

Table 2: Solubility data for the complexes

Compounds	H_2O	EtOH	MeOH	DCM	DMSO	DMF	Acetone	Diethylether
L_1	I	SS	S	SS	S	S	S	I
$[Cu(L_1)\ (bpy)\ (H_2O)_2]Cl$	I	S	S	I	S	S	S	I
$[Cu(L_1)\ (phen)\ (H_2O)_2]Cl$	I	S	SS	I	S	S	S	I
$[Ni(L_1)\ (bpy)\ (H_2O)_2]Cl$	I	S	S	SS	S	S	S	I
$[Ni(L_1)\ (phen)\ (H_2O)_2]Cl$	I	S	S	I	S	S	SS	I
L_2	I	S	S	SS	S	S	S	SS
$[Cu(L_2)\ (bpy)\ (H_2O)_2]Cl$	I	S	S	I	S	S	S	I
$[Cu(L_2)\ (phen)\ (H_2O)_2]Cl$	I	S	S	I	S	S	SS	I
$[Ni(L_2)(bpy)]Cl$	I	S	S	I	S	S	S	I
$[Ni(L_2)(phen)]Cl$	I	S	S	I	S	S	S	I

I: Insoluble, S: Soluble, SS: Sparingly soluble

Infrared Spectra

The structurally significant IR bands for free ligand and its complexes are reported in Table 3. The diagnostic and relevant vibrational frequencies obtained from the spectra of the compounds are assigned to fundamental vibrational modes based on literature reports on similar compounds (Deepa and Aravindakshan, 2005; Singh and Singh, 2012). The infrared spectra of the ligands were compared to that of the metal complexes to observe the shifts in bands which could provide an evidence of coordination to the metal ion (Neelammaa *et al*, 2010).

In the synthesized hydrazone ligands (L_1 and L_2), the bands at 3441 cm^{-1} and 3485 cm^{-1} are assigned to ʋ(OH/H_2O) vibrational frequency for both L_1 and L_2 respectively while the band at 3244 cm^{-1} in L_1 and 3242 cm^{-1} in L_2 is assigned for ʋ(N-H) vibrational frequencies. The carbonyl stretching frequencies band ʋ(C=O) occurred at 1639 and 1637 cm^{-1} for L_1 and L_2 respectively.

The azomethine bands ʋ(C=N) which is the other point of coordination occurs in the range 1514 to 1541 cm^{-1} for the ligands, while the bands at 1024 cm^{-1} and 1022 cm^{-1} are assigned to ʋ(N-N) vibrational frequencies of 2-ABH and VBH respectively. On complexation, there was the disappearance of the ʋ(C=O) and the ʋ(N-H) bands in both ligands as a result of enolization and subsequent deprotonation which suggest that the ligands coordinated to the metal ion in enol form. A comparison of the infrared spectra of the ligands and its metal complexes mixed with 2,2-bipyridine and 1,10-phenanthroline (Table 3) reveals that the ligands are mononegative bidentate, coordinating via the azomethine nitrogen (C=N) and deprotonated carbonyl oxygen ($=C-O^-$) which is evident in the appearance of a new band at 1145-1282 cm^{-1} due to (C=N-N=C) in all the mixed metal complexes.

The azomethine band ʋ(C=N) had a shift ranging from 5 to 50 cm^{-1} in the complexes which is indicative of the coordination through the azomethine nitrogen ʋ(C=N) bond to the metal ions. (Chandra and Kumar, 2005). The ʋ(N-N) vibrational frequency for both 2-ABH and VBH shifted on complexation as a result of decrease in electron density on the nitrogen atom. The appearance of new bands in the low frequency region at 536-650 cm^{-1} and 418-447 cm^{-1} are attributed to metal to oxygen (M-O) and metal to nitrogen (M-N) bonds respectively are evidence of coordination (Abdel-Aziz *et al.*, 2009). Typical IR spectra of VBH (L_2) and mixed Cu(II) complex are displayed in Figures 2 (Appendix).

Table 3: Infrared spectra data (cm^{-1}) of the hydrazones and their mixed metal (II) complexes

Compounds	υ(O-H)	υ(N-H)	υ(C=O)	υ(C=N)	υ(C=N)$_{(base)}$	υ(N-N)	υ(M-O)	υ(M-N)
L1		3244m	1639m	1541m	-	1024w	-	-
[Cu(L_1) (bpy) (H_2O)$_2$]Cl	3443b	-	-	1568m	1473m	1026w	636w	418w
[Cu(L_1) (phen) (H_2O)$_2$]Cl	3456b	-	-	1516m	1464m	1047w	644w	428w
[Ni(L_1) (bpy) (H_2O)$_2$]Cl	3441b	-	-	1492m	1435m	1033w	536w	447w
[Ni(L_1) (phen) (H_2O)$_2$]Cl	3450b	-	-	1492m	1435 m	1033w	650w	418w
L_2	3485m	3242s	1637m	1514m	-	1022w	-	-
[Cu(L_2) (bpy) (H_2O)$_2$]Cl	3491b	-	-	1568m	1496m	1026w	634w	418w
[Cu(L_2) (phen) (H_2O)$_2$]Cl	3448b	-	-	1526m	1516m	1047w	644w	430w
[Ni(L_2)(bipy)]Cl	3491b	-	-	1595m	1512m	1039w	557w	418w
[Ni(L_2)(phen)]Cl	3491b	-	-	1595m	1512m	1039w	557w	418w

Electronic spectra

The solution electronic spectra measured in methanol for the synthesized hydrazone ligands and their mixed metal (II) complexes are presented in Table 4. In the ultraviolet spectra of the synthesized ligands (L_1 and L_2), two electronic transitions were prominent. The bands in the range 30,487 to 30,674 cm^{-1} have been assigned to the $\pi \rightarrow \pi^*$ transition in the aromatic system (Singh *et al*, 2009; Abdel-Wahab *et al*, 2011). The bands in the range 33,333 to 34,965 cm^{-1} and 33,112 to 33,333 cm^{-1} are attributed to the second intraligand transition $n \rightarrow \pi^*$ in the azomethine moiety (Al-sha'alan, 2007; Babahan *et al.*, 2013). Vanillin-benzoylhydrazone (L_2) showed an additional band at 43,103cm^{-1} which is assigned to high energy transition $n \rightarrow \sigma^*$ due to excitation of the oxygen lone pair of electron to the antibonding sigma orbital of the hydroxyl group (Dandawante *et al,* 2012). Upon coordination with complexes of Cu(II) and Ni(II) mixed with 2,2-bipyridine and 1,10-phenathroline, these intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition in the free, uncoordinated L_1 and L_2 ligands undergo shift in the UV spectra suggesting a strong interaction between the ligands and the metal ion. The visible spectra of [Cu(L_1)(bpy)(H_2O)$_2$]Cl, showed one broad, d-d band centered at 14,306 cm^{-1} and a slight shoulder at 13,422 cm^{-1} as a result of distortion, while [Cu(L_1)(phen)(H_2O)$_2$]Cl showed a band at 14,619 cm^{-1}. This is consistent with the $^2E_g \rightarrow {}^2T_{2g}$ transition in an octahedral environment (Parrilha *et al*, 2010). The broadening of the band may be due to Jahn-Teller effect arising from unequal occupation of the e_g pair of orbitals. The visible spectra of all the mixed nickel(II) complexes showed three d-d bands at 15,625 cm^{-1}, 14,084 cm^{-1} and 11,834 cm^{-1} respectively, which are expected for a nickel(II) ion in an octahedral environment corresponding to the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ in the range 11,834 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{1g}$ in the range 14,084 - 15,625 cm^{-1} (Cotton *et al*, 2003; Singh and Singh, 2012). Three d-d bands were also observed for Ni(II) complexes of 2-ABH mixed with 2,2-bipyridine at 14,409, 12,821 and 11,710 cm^{-1} which are also expected for Ni(II) ion in octahedral environment. However, the visible spectra of [Ni(L_2)(bpy)]Cl and [Ni(L_2)(phen)]Cl displayed two d-d bands observed at 19,231 and 15,385 cm^{-1} and at 15,503 and 13,333 cm^{-1} respectively, which are consistent with square planar geometry and are assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) and $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$) electronic transitions respectively (Gup and Kirkan, 2006; Lima *et al.*, 2008). Typical ultraviolet and visible spectra of these complexes are displayed in Figures 3 (Appendix).

Table 4: UV-VIS spectral data of free ligands and their mixed metal complexes

Compounds	Intraligands transition (cm^{-1})	Charge transfer (cm^{-1})	Ligand field transition (cm^{-1})	Assignment	Proposed structure
L_1	30,674, 33,333- 34,965				
$[Cu(L_1)(bpy)(H_2O)_2]Cl$	32,051, 33,112,		14,450	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
$[Cu(L_1)(phen)(H_2O)_2]Cl$	34,013, 36,496		14,164	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
$[Ni(L_1)(bpy)(H_2O)_2]Cl$	34,482, 33,112, 30,487		14,409, 12,821, 11,710	$^3A_{2g}$ (F)$\rightarrow {}^3T_{1g}$(P) $^3A_{2g}$(F)$\rightarrow {}^3T_{1g}$(F) $^3A_{2g}$(F)$\rightarrow {}^3T_{2g}$(F)	Octahedral
$[Ni(L_1)(phen)(H_2O)_2]Cl$	34,722, 33,333, 30,120		15,625, 14,084, 11,834	$^3A_{2g}$ (F)$\rightarrow {}^3T_{1g}$(P) $^3A_{2g}$(F)$\rightarrow {}^3T_{1g}$(F) $^3A_{2g}$(F)$\rightarrow {}^3T_{2g}$(F)	Octahedral
L_2	30,488, 33,333, 43103				
$[Cu(L_2)(bpy)(H_2O)_2]Cl$	40,816, 33,333, 32,258	47,619	14,327	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
$[Cu(L_2)(phen)(H_2O)_2]Cl$	37,037, 33,898		14,286	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
$[Ni(L_2)(bpy)]Cl$	28,986	45,455	19,231 15,385	$^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
$[Ni(L_2)(phen)]Cl$	29,412	47,619	15,503 13,333	$^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar

Magnetic susceptibility measurements

The room temperature magnetic susceptibilities and effective magnetic moments of the mixed metal complexes prepared are given in Table 5. The magnetic moment of low-spin d^8 nickel(II) complexes is expected to be zero and diamagnetic with a square planar geometry. The effective magnetic moment for the synthesized nickel(II) complexes of vanillinbenzoylhydrazone (L_2) mixed with 2,2^1-bipyridine and 1,10-phenanthroline showed a magnetic moment of 0.49 B.M and 0.75 B.M respectively, these values are consistent for the d^8 diamagnetic electronic configuration with square planar geometry. The slight increase in these magnetic moments are indicative of a low spin-high spin equilibrium mixture with some paramagnetic nickel(II) species in accordance with the interpretation of Woods and Patel, 1990**.** The magnetic moment of 2.78 and 3.11 B.M for nickel(II) complexes of 2-anisaldehyde-benzoylhydrazone (L_1) mixed with 1,10-phenathroline and 2,2^1-bipyridine are consistent with those reported for octahedral geometry with d^8 electronic configuration having two unpaired electrons. The magnetic susceptibilities of the synthesized copper(II) complexes of 2-ABH (L_1) and VBH (L_2) mixed with 2,2^1-bipyridine and 1,10-phenanthroline are indicative of d^9 electronic configuration with one unpaired electron. The effective magnetic moment of 2.14 - 2.36 B.M observed for the complexes are close to the range of 1.70 to 2.20 B.M usually observed for magnetically dilute copper(II) complexes with octahedral geometry (Greenwood and Earnshaw, 1984; Figgis, 1978**).** This is suggestive of a strong ferromagnetic interaction between the adjacent magnetic centers (Emeleus and Sharpe, 2008).

Table 5: Magnetic susceptibility data of the mixed metal (II) complexes

Compounds	M.W g/mol.	$\chi_i \times 10^6$	$\chi_m \times 10^6$	Temp. (K)	μ_{eff}(B.M)
$[Cu(L_1)(bpy)(H_2O)_2]Cl$	545.50	-273.51	2313.61	295.5	2.21
$[Cu(L_1)(phen)(H_2O)_2]Cl$	569.52	-285.51	2480.57	295.5	2.14
$[Ni(L_1)(bpy)(H_2O)_2]Cl$	540.64	-263.51	3827.60	295.5	3.11
$[Ni(L_1)(phen)(H_2O)_2]Cl$	564.66	-285.51	2979.80	295.7	2.78
$[Cu(L_2)(bpy)(H_2O)_2]Cl$	561.50	-282.73	2363.68	296.0	2.25
$[Cu(L_2)(phen)(H_2O)_2]Cl$	585.52	-294.73	2065.43	296.0	2.36
$[Ni(L_2)(bpy)]Cl$	520.61	-282.73	-180.45	296.0	0.49
$[Ni(L_2)(phen)]Cl$	544.63	-294.66	-51.53	296.0	0.75

Conductivity measurement

The molar conductivities in DMF for all complexes are in the range 41.67–82.53 Ω^{-1} cm^2 mol^{-1}, indicating their electrolytic nature (Geary, 1971). These value showed that they are 1:1 electrolyte. The high values of molar conductance may be due to partial dissociation of the metal complexes in the solvent. The results obtained were in agreement with the proposed geometries for the metal complexes (Imran *et al.*, 2013). The molar conductivity measurements are displayed in Table 6.

Table 6: Conductivity measurement of the metal complexes in (Ω^{-1}cm^{2}mol^{-1})

Compounds	**$\Lambda m(\Omega^{-1}cm^2mol^{-1})$**	**Solvent**	**Electrolyte**
$[Cu(L_1)(bpy)(H_2O)_2]Cl$	62.87	DMF	1:1
$[Cu(L_1)(phen)(H_2O)_2]Cl$	63.52	DMF	1:1
$[Ni(L_1)(bpy)(H_2O)_2]Cl$	41.67	DMF	1:1
$[Ni(L_1)(phen)(H_2O)_2]Cl$	42.12	DMF	1:1
$[Cu(L_2)(bpy)(H_2O)_2]Cl$	70.48	DMF	1:1
$[Cu(L_2)(phen)(H_2O)_2]Cl$	59.96	DMF	1:1
$[Ni(L_2)(bpy)]Cl$	82.53	DMF	1:1
$[Ni(L_2)(phen)]Cl$	72.95	DMF	1:1

Antimicrobial Studies

The synthesized compounds were tested against eleven micro-organisms consisting of six Gram-Negative and five Gram -Positive bacterial. The antimicrobial activity was carried out using a concentration of 10 mg/ml of synthesized compounds while streptomycin and ampicillin antibiotic were used as standard at a concentration of 1mg/ml. DMSO was used as solvent and as a negative control. $[Cu(L_2)(phen)(H_2O)_2]Cl$ showed the highest level of activity against all the tested micro-organisms with the exception of *Klesiella. pneumonia* and *Proteus vulgaris*. This is reflective in the zone of inhibition exhibited against all the tested organisms. All the compounds showed significant antimicrobial activities against Gram Negative bacteria strains that had been found to be resistant to most drugs. The tremendous antimicrobial activity of compounds viz: $[Cu(L_1)(bpy)(H_2O)_2]Cl$, $[Cu(L_1)(phen)(H_2O)_2]Cl$, $[Cu(L_2)(phen)(H_2O)_2]Cl$, and $[Cu(L_2)(bpy)(H_2O)_2]Cl$ with the best antimicrobial activities could be due to the presence of heterocyclic compounds (2,2^1-bipyridine and 1,10-phenanthroline) in the complexes which by synergistic effect enhanced the inhibitory activity.

$[Ni(L_2)(phen)(H_2O)_2]Cl$ also had activity against the Gram Negative bacteria with the exception of *Pseudomonas flourescens*. Generally, the antimicrobial activities of all the synthesised compounds compare favourably with those of streptomycin and ampicillin used as the control and standard. The result for the zone of inhibition is shown in Table 7 while the graph showing the zone of inhibition of Ligands and metal complexes are displayed in Figures 4 and 5 respectively.

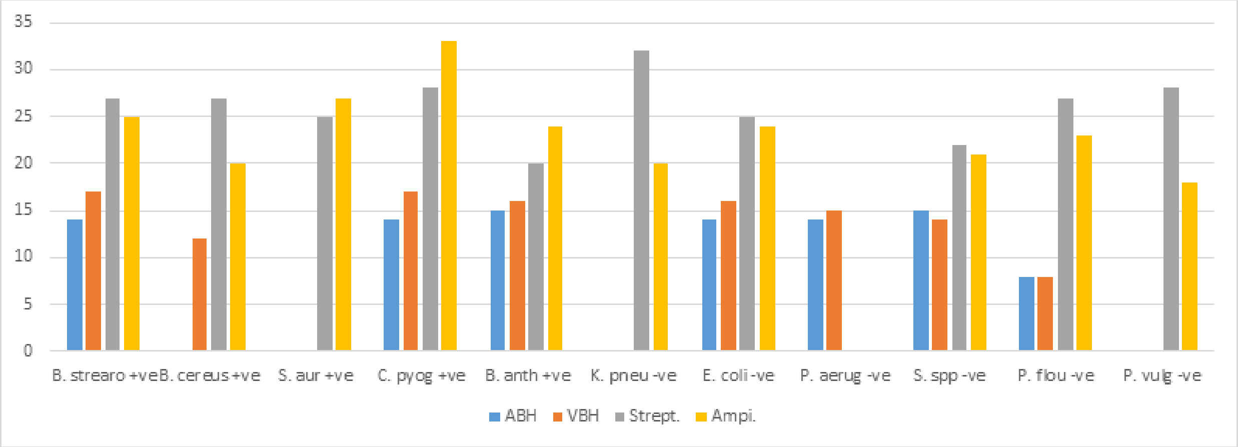


Figure 4: Graph of zone of inhibition of synthesized ligands against micro-organisms

Table 7: Antimicrobial activity data of the compounds (10 mg/ml) and controls.

					Growth inhibition zone in millimeter (mm)						
		Gram-positive				Gram-negative					
Compounds	*(B. strearo*	*B. cereus*	*S. aur*	*C. pyog*	*B. anth)*	*(K. pneu*	*E. coli*	*P. aerug*	*S. spp*	*P. flou*	*P. vulg)*
$[Cu(L_1)(bpy)(H_2O)_2]Cl$	0	11	9	18	10	0	10	0	10	6	0
$[Cu(L_1)(phen)(H_2O)_2]Cl$	0	20	0	32	0	0	14	12	12	7	0
$[Ni(L_1)(bpy)(H_2O)_2]Cl$	13	10	15	13	13	0	12	14	12	8	12
$[Ni(L_1)(phen)(H_2O)_2]Cl$	13	8	14	0	16	0	12	0	0	11	14
$[Cu(L_2)(bpy)(H_2O)_2]Cl$	32	29	13	37	20	0	23	16	21	20	0
$[Cu(L_2)(phen)(H_2O)_2]Cl$	25	8	18	28	15	17	13	16	16	16	17
$[Ni(L_2)(bpy)]Cl$	0	7	12	0	0	12	14	10	18	0	0
$[Ni(L_2)(phen)]Cl$	13	0	0	14	13	0	13	12	12	0	0
Streptomycin	27	27	25	28	20	32	25	0	22	27	28
Ampicillin	25	20	27	33	24	20	24	0	21	23	18

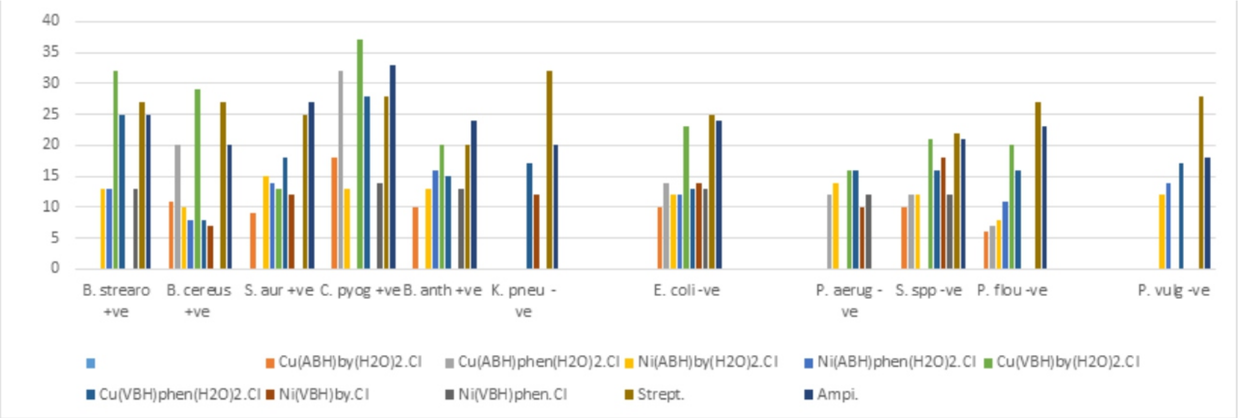


Figure 5: Graph of zone of inhibition metal complexes against micro-organi

CONCLUSIONS

Two hydrazone ligands 2-anisaldehyde-benzoylhydrazone (L_1) and vanillin-benzoylhydrazone (L_2), their mixed nickel (II) and copper (II) complexes with $2,2^1$-bipyridine and 1,10-phenanthroline (N-N bases) were prepared and characterized by physical and chemical methods. The nickel(II) complexes of the hydrazone ligands mixed with $2,2^1$-bipyridine and 1,10-phenathroline show colours ranging from deep green to orange while the colour of copper(II) complexes of the hydrazone ligands mixed with $2,2^1$-bipyridine and 1,10-phenathroline are generally green. The compounds are generally insoluble in water; they had a high melting point which revealed a high thermal stability of the complexes. Infrared spectra indicated that coordination of the ligands to the metal ions occurred via the azomethine nitrogen (C=N) and deprotonated carbonyl oxygen (=C?O-) suggesting that the ligands acted in a mononegative bidentate fashion. The percentage metal analysis suggested the stoichiometry of the mixed complexes to be 1:1:1 ratio for metal: ligand: $N\text{-}N_{(base)}$

The UV-VIS electronic spectra and magnetic moments for the mixed complexes of Ni(II) and Cu(II) suggested six coordinate octahedral geometries for the compounds with the exception of $[Ni(L_2)(bpy)]Cl$ and $[Ni(L_2)(phen)]Cl$ that had a probable four coordinate square planar geometry. This observation was supported by the conductivity measurement values which revealed that the chloride ion is outside the coordination sphere.

The mixed ligand complexes of copper displayed moderate activity against the tested micro-organisms where $[Cu(L_1)(bpy)(H_2O)_2]Cl$, $[Cu(L_1)(phen)(H_2O)_2]Cl$, $[Cu(L_2)(phen)(H_2O)_2]Cl$, and $[Cu(L_2)(bpy)(H_2O)_2]Cl$ had the best antimicrobial activities. This could be due to the presence of the heterocyclic bases (1, 10-phenanthroline and 2, 2^1-bipyridine) in the mixed metal (II) complexes which enhanced the biological properties by synergistic effect.

PROPOSED STRUCTURES

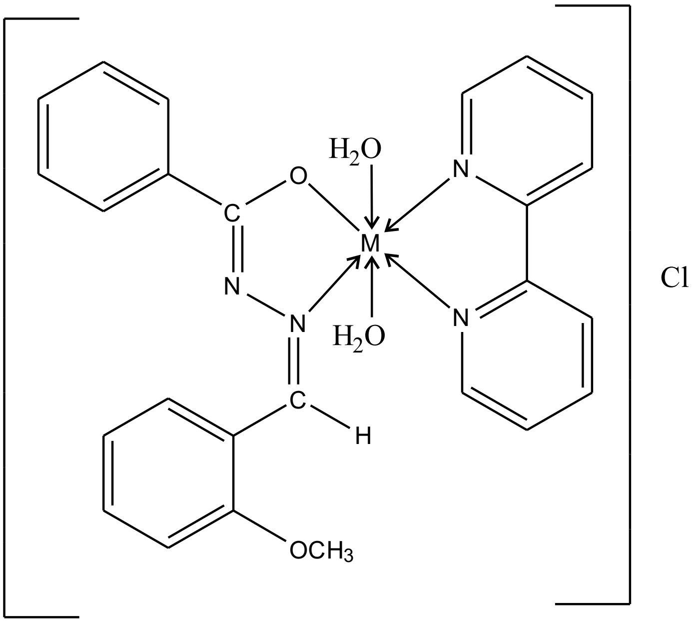


Figure 5: Proposed structure for $[Cu(L_1)(bpy)(H_2O)_2]Cl$ and $[Ni(L_1)(bpy)(H_2O)_2]Cl$

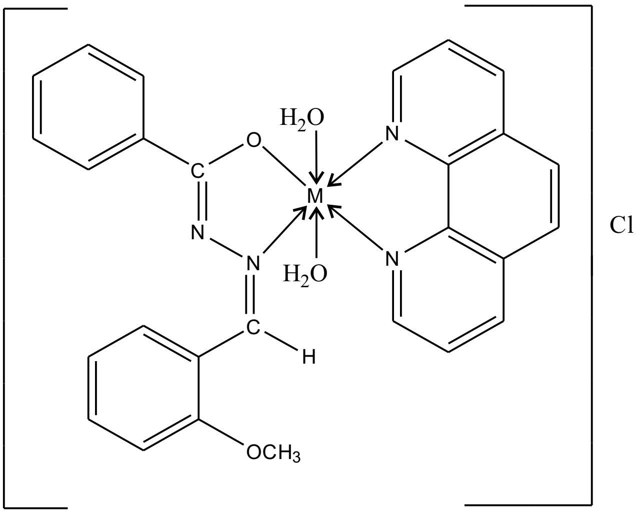


Figure 6: Proposed structure for [Cu(L_1)(phen)(H_2O)$_2$]Cl, and [Ni(L_1)(phen)(H_2O)$_2$]Cl

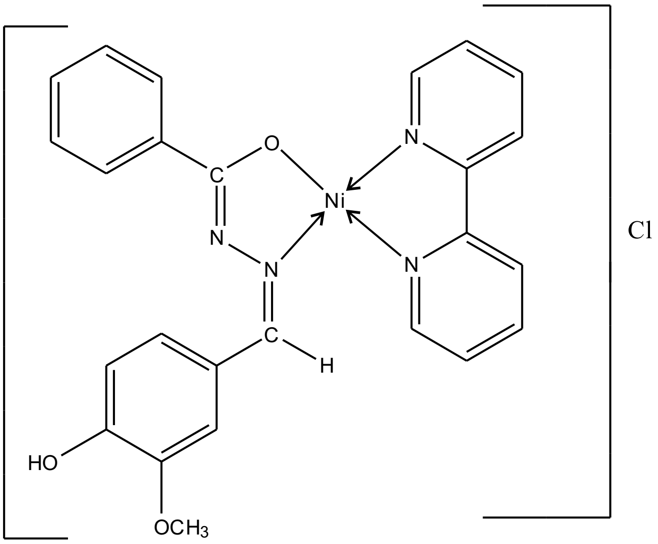


Figure 7: Proposed structure for [Ni(L_2)(bpy)]Cl

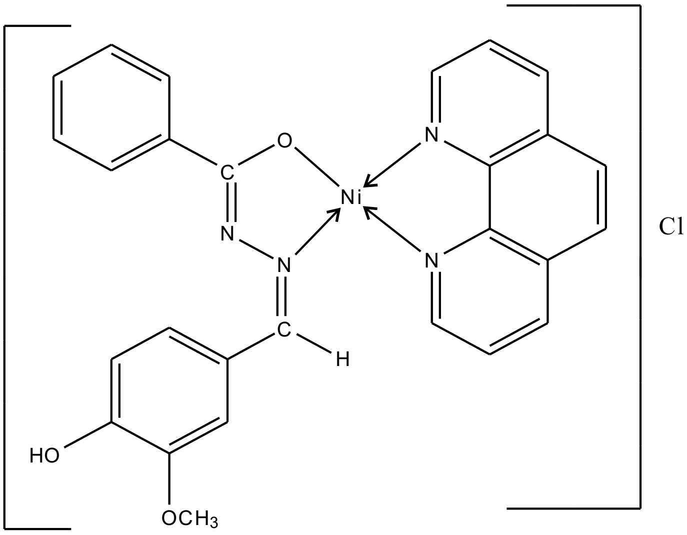
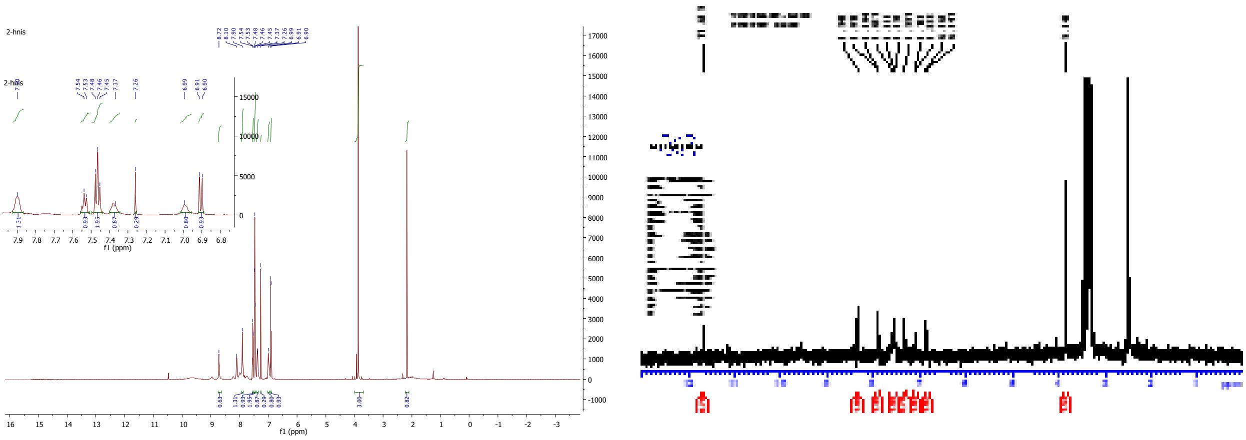


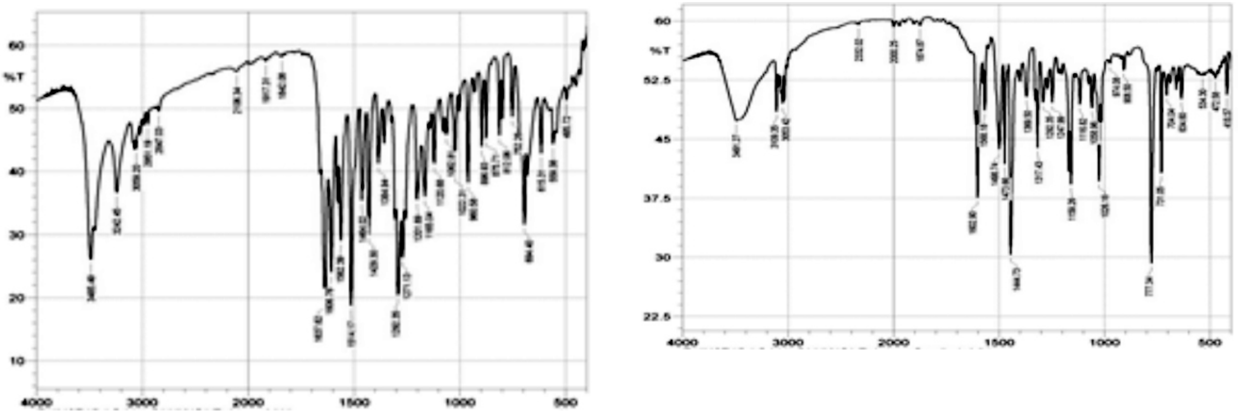
Figure 8: Proposed structure for [Ni(L_2)(phen]Cl.

APPENDICES



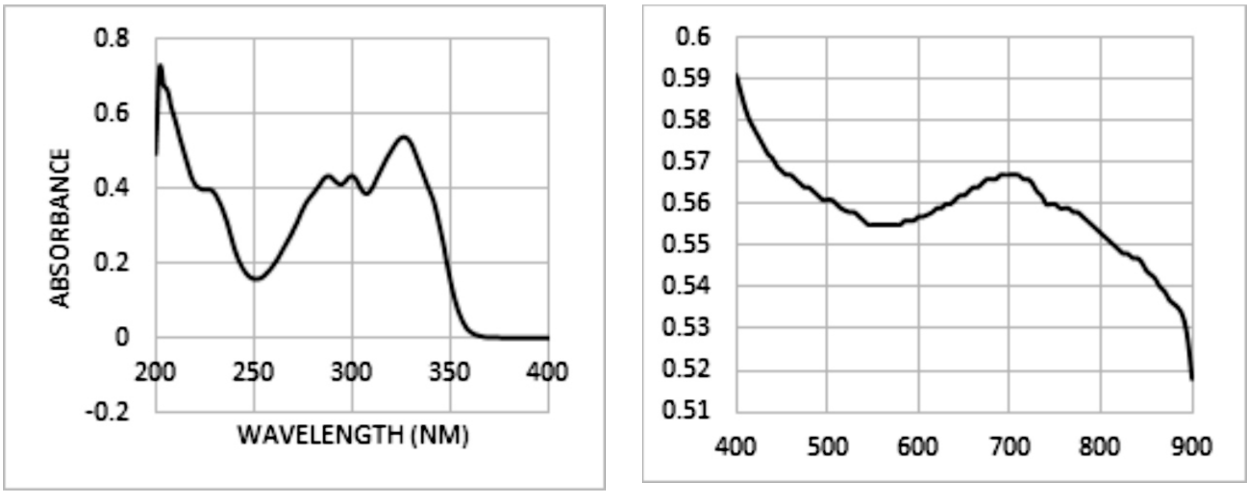
(a) (b)

Figure 1: (a) ^{1}HNMR of 2-anisaldehyde-benzoylhydrazone (L_1) and (b) vanillin-benzoylhydrazone (L_2)



(a) (b)

Figure 2. IR spectra of vanillin benzoylhydrazone (L_2) (a) and $[Cu(L_2)(bpy)(H_2O)_2]Cl$ (b).



(a) (b)

Figure 3 (a) UV of anisaldehyde –benzoylhydrazone (2-ABH); Visible spectrum of $Cu(ABH)(bpy)(H_2O)_2.Cl$ (b)

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