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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND Mn(II), Co(II), Ni(II) and Cu(II) COMPLEXES OF SOME HYDRAZONES AND NITROGEN DONOR LIGANDS

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ABSTRACT

Mn(II), Co(II), Ni(II) and Cu(II) mixed ligand complexes of some Benzoyl hydrazones (hydrazide Schiff bases) with 1,10-Phenanthroline (Phen), 2,2'-bipyridine and ethylenediamine(en) were synthesized and characterized using metal analysis, molar conductivity, magnetic susceptibility, electronic spectra, infrared measurement and antimicrobial activity. The percentage metals of the complexes are in close agreement with their corresponding theoretical values. The molar conductance of some of the complexes that were soluble in nitromethane reveals that only $[Co(H_1L)_2Bipy]Cl_2$ ***is a 1:2 electrolyte while*** $[Cu(Phen)(H_1)](NO_3)H_2O$, $[Cu(Bipy)H_1L]NO_3$, $[Cu(Phen)H_1L]NO_3$, $[Cu(H_1L)(H_1A)(NO_3)H_2O]NO_3$, ***and*** $[Cu(H_1HY)(H_1A)(NO_3)H_2O].NO_3.2H_2O$ ***are 1:1 electrolyte. The electronic spectra displayed bands which were assigned to*** $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, ***Charge transfer and d-d transitions. From the d-d transitions in the visible region of the spectra, it was suggested that these complexes have four-, five- and six- coordinate stereochemistries. The proposed geometries were backed up by the observed magnetic moments which were in line with the expected or theoretical values. The infrared spectra gave bands that were assigned to ν(NH), azomethine ν(C=N) and ν(C=O) vibrational frequencies. The shift in the ν(C=O), ν(N-N), ν(NH), ν(C-N) and ν(C=N) bands in the spectra of the complexes reveals that there is coordination of the ligands to the metal centre. The complexes compared favourably well with Gentamicin and Ketoconazole with respect to antibacterial and antifungal activities respectively.***

Keywords: *Hydrazones, nitrogen donor ligands, metal (II), spectral measurements, antimicrobial studies*

INTRODUCTION

There has been considerable interest in the synthesis of Hydrazones which is an important class of Schiff base ligands because they exhibit wide variety of biological activities such as antimicrobial, anticonvulsant, antidepressant, anti-inflammatory, analgesic, antiplatelet, antimalarial, anticancer, antifungal, antitubercular, antiviral and cardio protective (Chaston *et al,* 2004; Kaan *et al,* 2019; Aly and Fathalla, 2020). Some Metal complexes of hydrazones derivatives are found to be highly cytotoxic to human tumor cell lines (Recio Despaigne et al., 2012; Angel et al., 2014; Ferreira *et al.,* 2016; Dominik *et al.,* 2017; Jiayang *et al.,* 2019).

The bonding of hydrazone ligands with transition metals may proceed through the ketonic form or the enolic form, leading to the formation of two types of complexes. The nature of the metal ion, anion of the salt and alkalinity of the reaction medium determine the mode of bonding of hydrazone and molecular structure of the resulted complexes (Shakdofa *et al,* 2015).

In a study, hydrazones were found to be effective in inhibiting corrosion because their construction contains two nitrogen atoms and an imine bond which act as active adsorption centres (Turuvekere et al., 2016). Aryl-hydrazone transition metal complexes have been reported to give useful models to elucidate the role of hydrazone derivatives in the enzyme inhibition mechanisms and for their possible applications in the pharmacological field (Ray, et al. 2008).

The cytotoxic action of some metal (II) complexes was carried out and compared to that of the anticancer drug doxorubicin. Results revealed that one of the compounds has a wide range of cytotoxicity against the three cell lines in concentration ranges as that of doxorubicin (El-Saied et al., 2018). Biological studies on the synthesized Cu(II), Ni(II) and Co(II) complexes of hydrazone-oxime ligands derived from 3-(hydroxyimino) butan-2-one showed good to excellent biological activity with aspergillius niger (Shakdofa et al., 2018). The complexes of hydrazone possess important biological and chemical properties (Salah et al., 2019). In silico docking and in vitro antibacterial activities of novel hydrazone complexes were investigated and the results showed that nickel complexes have the highest antimicrobial activity (Salah *et al.,* 2019).

A large number of mixed-ligand metal (II) complexes were recently reported (Salah *et al.,* 2019; Shakdofa *et al.,* 2018) and many of them showed prominent anticancer activity (Gou et al., 2017) but there is little or no information on the synthesis of mixed-ligand metal (II) complexes with nitrogen containing ligands. Herein we report the synthesis of different Benzoyl hydrazones and their metal (II) complexes and characterize them using metal analysis, molar conductivity, magnetic susceptibility, electronic spectra, infrared measurement and antimicrobial studies.

EXPERIMENTAL

Materials and physical measurements

The reagents used were of analytical grade. They are Ethyl benzoate, hydrazine hydrate, ammonia/ ammonium chloride buffer, nitric acid, perchloric acid, ethylenediaminetetraacetic acid, zinc sulphate heptahydrate, copper nitrate trihydrate, manganese sulphate monohydrate, cobat (II)chloride hexahydrate, salicylaldehyde, m-nitrobenzaldehyde, m-hydroxybenzaldehyde, p-Anisaldehyde. The % metals in the mixed-ligand complexes were determined by titrimetric method with EDTA. The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech). The infrared spectra of the complexes, as pressed KBr disc, were recorded on the Buck 500 Scientific model infrared spectrophotometer in the region 4000-400 cm^{-1}. The solution spectra of the complexes in chloroform and methanol were recorded on a Spectro UV-VIS double beam PC scanning spectrophotometer–UVD-2960.The electronic reflectance spectra of the complexes in Nujol mulls were determined by a Genesys 10S v1.200 2L7H311008 UV-Spectrophotometer at a fast scan speed.

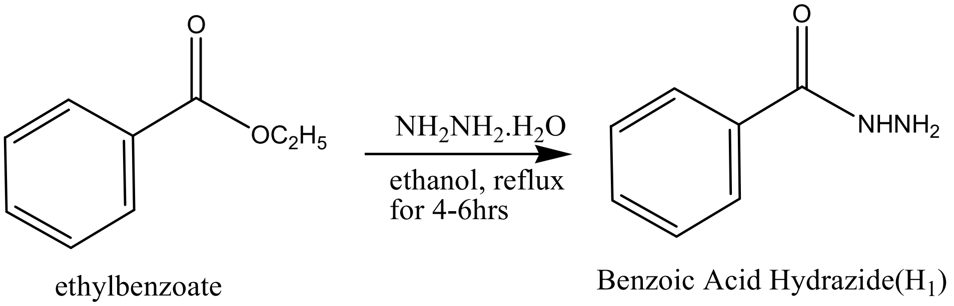
PREPARATION OF THE LIGANDS

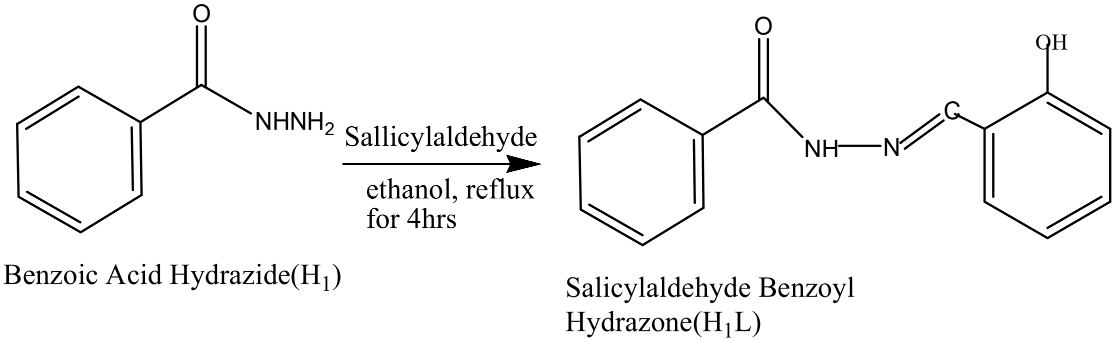
Synthesis of Benzoic acid Hydrazide (H_1)

A solution of ethyl benzoate (839 mmol) in 150 mL of ethanol and hydrazine hydrate (839 mmol) were refluxed in a 500 mL round bottom flask for 6 hours. The resulting mixture was kept standing overnight and concentrated by heating after which the hydrazide was precipitated out of solution. This was filtered by suction and washed using ethanol. The resulting precipitate was dried over silica gel.

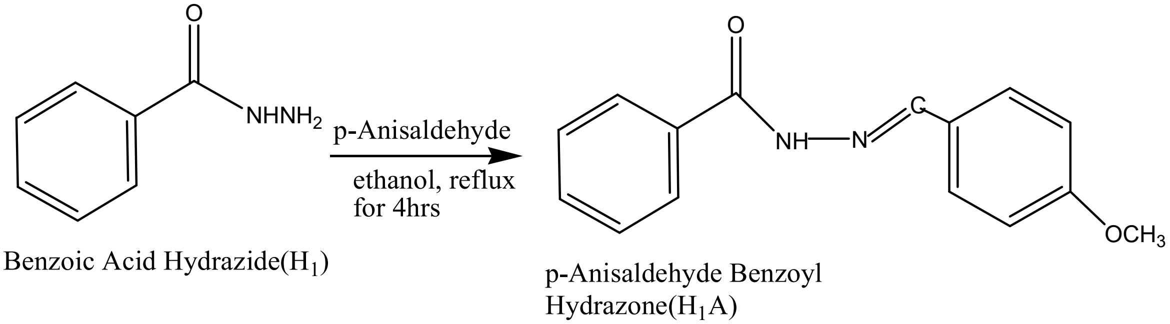
Synthesis of Salicyaldehyde Hydrazone (H_1L)

Benzoic acid hydrazide (3 g, 22 mmol) was dissolved in 20mL of ethanol and was left to reflux for few minutes for effective dissolution, after which (2.34mL, 22 mmol) of salicyaldehyde was added dropwisely and the solution was allowed to reflux for 4hours.





The resulting mixture was allowed to cool and left on the bench overnight to crystallize. Golden Yellow crystals were obtained; this was filtered by suction and dried in the desiccator over silica gel. Same Procedure was used to synthesize three other hydrazones.



Synthesis of p-Anisaldehyde Hydrazone (H_1A)

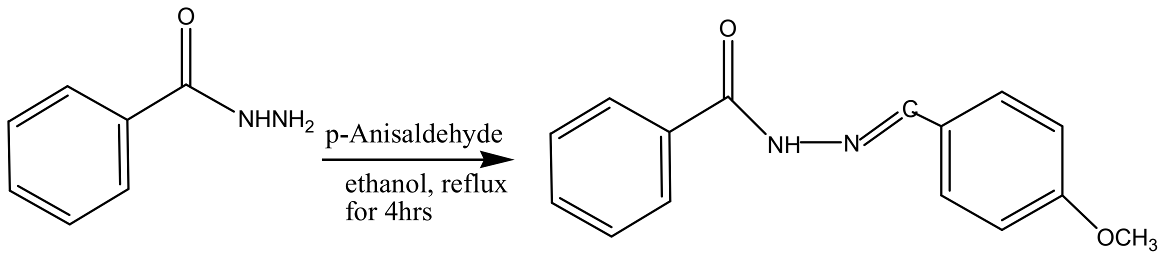
p-Anisaldehyde Hydrazone was prepared using a similar procedure as the three other hydrazones above with the following materials: Benzoic acid Hydrazide (6 g, 44 mmol), p-Anisaldehyde (5.3571mL, 44 mmol) and a white precipitate was obtained.

Synthesis of m-Nitrobenzaldehyde Hydrazone (H_1N)

m-Nitrobenzaldehyde Hydrazone was prepared using a similar procedure as the three other hydrazones above with the following materials: Benzoic acid Hydrazide (6 g, 44 mmol), m-Nitrobenzaldehyde (6.6493 g, 44 mmol) and a light Yellow precipitate was obtained.

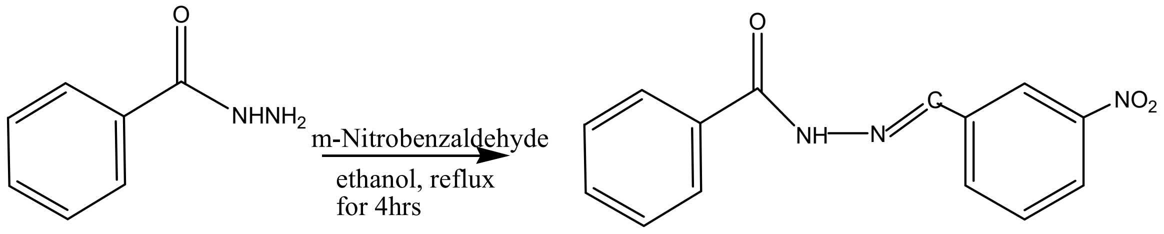
Synthesis of m-Hydroxybenzaldehyde Hydrazone (H_1HY)

m-Hydroxybenzaldehyde Hydrazone was prepared using a similar procedure as the three other hydrazones above with the following materials: Benzoic acid Hydrazide (6 g, 44 mmol), m-Hydroxy benzaldehyde (5.3734 g, 44 mmol) and golden brown crystals were obtained.



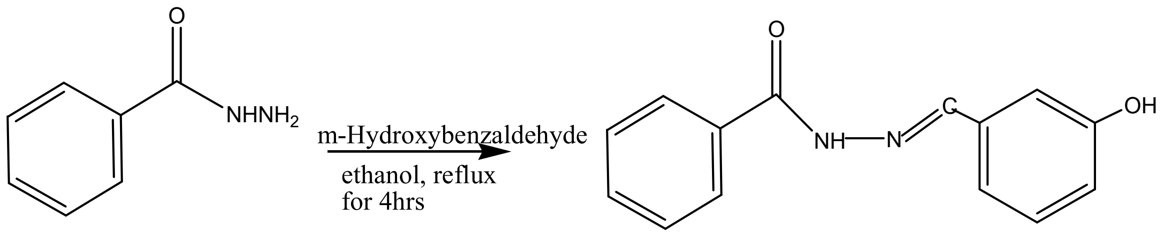
Benzoic Acid Hydrazide(H_1)

p-Anisaldehyde Benzoyl Hydrazone(H_1A)



Benzoic Acid Hydrazide(H_1)

m-Nitrobenzaldehyde Benzoyl Hydrazone(H_1N)



Benzoic Acid Hydrazide(H_1)

m-Hydroxybenzaldehyde Benzoyl Hydrazone(H_1HY)

PREPARATION OF COMPLEXES

Synthesis of [Cu(Phen)(H_1)](NO_3)H_2O

1,10-Phenanthroline (0.5 g, 2.522 mmol) was added to (0.3434 g, 2.522 mmol) of Benzoic acid Hydrazide(H_1) and 15mL of Ethanol was added to (0.6093 g, 2.522 mmol) $Cu(NO_3)_2.3H_2O$ in ethanol. The mixture was left to stir at room temperature for about two hours, a light blue precipitate was formed which was filtered by suction, washed with ethanol, distilled water and dried in a desiccator over silica gel.

Synthesis of [Cu(Phen)H_1L]NO_3

(0.2475 g, 0.8324 mmol) of 1,10-Phenanthroline and (0.3 g, 0.8324 mmol) of Salicylaldehyde hydrazone (H_1L) were added to 40mL of ethanol in a round bottom and the mixture was allowed to reflux for few minutes to aid effective mixing. (0.2 g, 0.8324 mmol) $Cu(NO_3)_2.3H_2O$ in ethanol was added dropwisely to it and the mixture was left to reflux for about 2hours. A dark green precipitate was obtained, after which it was filtered by suction, washed with ethanol and dried in a desiccator over silica gel.

Biological Studies

The antibacterial test was carried out at the Department of Pharmaceutical Microbiology, University of Ibadan, Ibadan, Nigeria.

Antimicrobial Susceptibility Testing

The antimicrobial activity of the synthesized compounds was determined by agar cup diffusion method using each compound in decreasing concentration of 100-6.25 mg/mL dissolved in either sterile distilled water or methanol against every microbial isolate tested. Plate cultures were prepared either by seeding (bacterial and yeast) or spread plate (moulds) using 0.1mL of 10-2 dilution from 18 -12 h-old broth culture of each bacterium or 24 to 72 h old broth of each fungus, in nutrient agar (bacteria) and sabouraud dextrose agar (fungi). Each of the wells dug in the set agar medial was filled with three drops of the dissolved compound, 100 mg/mL followed by pre-incubation diffusion period of 1 h. on bench. The cultured plates were incubated at 37 °C for 24 h (bacteria) and 28 °C for 24-72 h (fungi). Thereafter, the antimicrobial susceptibility was assessed by observing the plates for zones of growth inhibition, measures in mm (Omoregie *et al.,* 2015; Omoregie *et al.,* 2018).

RESULT AND DISCUSSION

The solubility of the complexes was tested in different solvents and it was observed that the complexes exhibit varying degrees of solubility in the solvents. It was observed that virtually all the complexes were insoluble in distilled water and n-hexane except $[Mn(H_1A)(en)(SO_4)(H_2O)]$ that is sparingly soluble. However, the complexes showed varying degrees of solubility in methanol, ethanol, acetone, nitromethane and chloroform. The molar conductances of some complexes that are soluble in nitromethane were obtained. The complexes are $[Cu(Phen)(H_1)](NO_3)H_2O$, $[Cu(Bipy)H_1L]NO_3$, $[Cu(Phen)H_1L]NO_3$, $[Co(Bipy)(H_1L)_2]Cl_2$, $[Cu(H_1L)(H_1A)(NO_3)H_2O]NO_3$, and $[Cu(H_1HY)(H_1A)(NO_3)H_2O].NO_3.2H_2O$. All these complexes are 1:1electrolytes except $[Co(Bipy)(H_1L)_2]Cl_2$ which is a 1:2 electrolyte. The magnetic moment of 1.73 BM of $[Cu(Phen)(H_1)]NO_3$, is in line with the expected value for magnetically dilute copper(II) compounds (Patel and Woods., 1990). The observed magnetic moment of the Ni^{2+} complexes at 2.8-3.1 BM corresponds to the theoretical value for Ni^{2+} in an octahedral field except for the case of $[Ni(H_1HY)(H_1A)]$ where obtained value (0.94 BM) shows that the complex is diamagnetic and this corresponds to a square planar geometry (Stone and Dori,1971). The observed magnetic moment value of 6.1 BM in $[Mn(H_1A)(en)(SO_4)(H_2O)]$ is in line with the expected value for a high spin Mn^{2+} (d^5) in an octahedral field (Syiemlieh *et al.*, 2018)

Infrared Spectra

The relevant infrared spectra data of the prepared ligands and complexes are presented in Table 2. The IR spectra of the five ligands (Benzoic acid Hydrazide (H_1) and four different Hydrazone; Salicylaldehyde hydrazone (H_1L), p-Anisaldehyde Hydrazone (H_1A), m-hydroxylbenzaldehyde Hydrazone (H_1HY) and m-Nitrobenzaldehyde Hydrazone (H_1N)) differ by the absence or presence of some bands depending on the functionalities present. The spectrum of Benzoic acid Hydrazide (H_1) show three bands assigned to both ν(NH) and $\nu(NH_2)$ vibrational frequencies 3299, 3198 and 3152cm^{-1} as compared to the single ν(NH) band observed in the Hydrazones (Alhadi, *et al.,* 2012).

Salicylaldehyde hydrazone (H_1L) spectrum differ from the spectrum of p-Anisaldehyde Hydrazone (H_1A) and m-Nitrobenzaldehyde Hydrazone (H_1N) by the presence of a broad band at 3444cm^{-1} assigned to the ν(OH) vibrational frequency. The presence of this band in the spectrum of m-hydroxylbenzaldehyde Hydrazone (H_1HY) makes them similar but they differ in the position of the ν(OH) band. This band is present in the spectrum of H_1HY around 3413cm^{-1}. However, H_1N differs from the other Hydrazones by the absence of a ν(C-O) band and the presence of a $\nu(NO_2)$ band at 1461cm^{-1} which is absent in the rest (Nakamoto *et al.,* 1958).

Table 1: Analytical and physical data of mixed ligand Mn(II), Co(II), Ni(II) and Cu(II) complexes of some hydrazones and nitrogen donor ligands

Compound	**Mol. wt.(g mol^{-1})**	**% Yield**	**%Metal Exp (Cal)**	**M.pt (^{o}C)**	**μ_{eff} (BM)**	**Colour**	**Cond. ($\Omega^{-1}cm^2$ mol^{-1})**
H_1	136.15	52.5	_	117-119	_	White	_
H_1L	240.26	52.5	_	170-172	_	Golden Yellow	–
H_1A	254.28	49.2	_	157-159	_	White	_
H_1HY	240.26	77.7	_	204-206	_	Golden Brown	–
H_1N	269.26	85.5	_	191-193	_	Light Yellow	–
$[Cu(Phen)(H_1)](NO_3)$ H_2O	458.87	31.2	14.51(13.83)	194-195	1.73	Light Blue	70
$[Cu(Bipy)H_1L]$ NO_3	520.94	55.5	12.72(12.19)	105-107		Green	70
$[Cu(Phen)H_1L]$ NO_3	544.96	47.0	12.42 (11.65)	260-262		Green	69
$[Ni(Bipy)H_1LNO_3]$	516.15	23.0	11.37 (12.30)	>300	2.9	Brownish-Yellow	–
$[Ni(Phen)H_1L(NO_3)]$	540.17	31.3	11.07(10.87)	> 300	3.1	Bright Yellow	–
$Ni(H_1L)(en)(NO_3)].3H_2O$	474.12	57.2	12.41(12.38)	> 300		Bright Yellow	–
$[Co(Bipy)(H_1L)_2]Cl_2$	766.64	46.1	7.27(7.69)	>300		Brownish-Green	210
$[Co(Phen)(H_1L)_2]$	719.61	29.2	7.62(8.19)	166-168		Dark Brown	–
$[Mn(Bipy)(H_1L)_2]6H_2O$	797.75	39.7	6.27(6.89)	282^d		Pale-Yellow	–
$[Mn(Phen)(H_1L)_2]$ $6H_2O$	821.77	39.9	5.80(6.69)	>300		Pale-Yellow	–
$[Cu(H_1HY)(H_1A)(NO_3)H_2O]. (NO_3)2H_2O$	736.10	70.2	8.25(8.63)	100-102		Dark Brown	70
$[Ni(H_1HY)$ $(H_1A)]$	551.23	26.5	10.92(10.65)	248-250	0.94	Orange	_
$[Cu(H_1L)(H_1A)(NO_3)$	700.06	58.6	9.61(9.07)	143-145		Green	70

$H_2O]$ NO_3							
$[Cu(H_1N)_2(NO_3)_26H_2O$	834.14	24.6	6.83(7.61)	229-231		Light Brown	–
$[Cu(H_1N)(H_1A)(NO_3)_2]$	711.04	45.9	9.29(8.93)	291-293		Light Brown	–
$[Cu(H_1N)(en)(NO_3)_2]$.	516.86	24.9	12.48(12.29)	258-260		Light Brown	–
$[Cu(H_1HY)(en)(NO_3)_2]6H_2O$	595.98	52.8	9.96(10.65)	174-176		Dark Brown	–
$[Mn(H_1A)(en)(SO_4)(H_2O)]$	483.38	43.3	11.64(11.37)	> 300	6.1	Dark Brown	–

Compared to the Spectrum of H_1 ligand that has three bands assigned to both v(NH) and v(NH_2) vibrational frequencies, $[Cu(Phen)(H_1)](NO_3)H_2O$ has two bands but are somewhat shifted to a higher frequency around 3317cm^{-1} and 3248cm^{-1}. The v(C=O) band seen in the ligand at 1659cm^{-1} was observed in the complex at a higher frequency at 1712cm^{-1}. The Salicylaldehyde Hydrazone (H_1L) spectrum has bands at 3444, 3268, 1606, 1673, 1141 and 1273cm^{-1} which were assigned to the v(OH), v(NH), v(C=N), v(C=O), v(C-O), v(N-N) and v(C-N) stretching vibrations respectively (Alhadi, *et al.,* 2012). These bands are observed in the various metal complexes but are somewhat shifted due to coordination to the metal centre. However, the disappearance of v(NH) and v(C=O) implies tautomerization.

This Salicylaldehyde Hydrazone (H_1L) can act both as a tridentate and bidentate ligand. It acted as a tridentate ligand by coordinating to metal centre by using the C=O, C=N (Azomethine) and OH binding sites (Popov *et al.,* 2007). An example of this case is seen in $[Cu(Bipy)H_1L]NO_3$, $[Cu(Phen)H_1L]NO_3$, $[Ni(Bipy)H_1L(NO_3)]$, $[Ni(Phen)H_1L(NO_3)]$ and $[Ni(H_1L)(en)(NO_3)].3H_2O$. In cases where the OH site is not used, then it can act as a bidentate ligand, examples are $[Co(Bipy)(H_1L)_2]Cl_2$, $[Co(Phen)(H_1L)_2]$, and $[Mn(Bipy)(H_1L)_2]6H_2O$ (El-Asmy et al., 2013). In the spectra of $[Cu(Bipy)H_1L]NO_3$ and $[Cu(Phen)H_1L]NO_3$ the disappearance of the v(NH) and v(C=O) bands was due to tautomerism (Mandal and Patel, 2017). In $[Co(Bipy)(H_1L)_2]Cl_2$ and $[Co(Phen)(H_1L)_2]$, the presence of the v(OH) band shows that there is no coordination at OH site of the ligand.

The bands in the range 721-727 cm^{-1} are out of plane motion of the hydrogen atoms on the heterocyclic rings and those within the range 845-849 cm^{-1} are hydrogen atoms on the middle ring (Omoregie et al., 2015). The bands in the range 756-759 cm^{-1} in the prepared bipyridine complexes are assigned as out of plane bending of ring hydrogens (Omoregie et al., 2015).

Electronic Spectra

The electronic spectra in chloroform and methanol and the solid reflectance spectra of the synthesized ligands and complexes are presented in tables 3 and 4. The Ligand Spectra of all the five ligands (H_1, H_1L, H_1A, H_1N and H_1HY) display bands that are assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. The $\pi\rightarrow\pi^*$ transitions observed ranges from 47,847-31,056cm^{-1} and the $n\rightarrow\pi^*$ transitions are in the range of 29,586-26,525 cm^{-1}.

Table 2: Infrared Spectra Data of mixed ligand Mn(II), Co(II), Ni(II) and Cu(II) complexes of some hydrazones and nitrogen donor ligands

Compound	**ν(OH) (cm^{-1})**	**ν(NH)/ ν(NH_2) (cm^{-1})**	**ν(C=O) (cm^{-1})**	**ν(C=N) (cm^{-1})**	**ν(C-N) (cm^{-1})**	**ν(N-N) (cm^{-1})**	**δ(Bipy) /Phen (cm^{-1})**	**ν(NO_2) (cm^{-1})**	**ν(SO_4) (cm^{-1})**
H_1	_	3299 3198 3152	1659	_	1120	986			
H_1L	3444	3268	1673	1606	1273	1078			
H_1A	_	3194	1640 1605	1570	1258	1023			
H_1HY	3413	3263	1634	1589	1293	966			
H_1N	_	3223	1645	1605	1288	1075	_	1461	_
$[Cu(Phen)(H_1)](NO_3)H_2O$	3415	3317 3248	1712	_	1146	996	848 721		_
$[Cu(Bipy)H_1L]NO_3$	_	_	_	1576	_	1087	756		
$[Cu(Phen)H_1L]NO_3$	_	_	_	1587	_	1035	849 723		
$[Ni(Bipy)H_1LNO_3]$	_	3125	1602	1564	1299	1040	757		_
$[Ni(Phen)H_1L(NO_3)]$	_	3138	1603	1565	1253	1039	846 721 **735**		
$[Ni(H_1L)(en)(NO_3)].3H_2O$	3385	3131	1604	1565	1256	1082			
$[Co(Bipy)(H_1L)_2]Cl_2$	3419	3154	1657	1611	1277	1035	759		
$[Co(Phen)(H_1L)_2]$	3436	3136	1641	1597	1270	1098	845 725 **753**		
$[Mn(Bipy)(H_1L)_2]6H_2O$	3385	3267	1668	1595	1260	983	764		1105
$[Mn(Phen)(H_1L)_2]\ 6H_2O$	3275	3123	1668	1576	1271	1081	857 727 **727**		1106
$[Cu(H_1HY)(H_1A)(NO_3)H_2O]$	3423	3197	1603	1559	1265	1062	_		

$.(NO_3)2H_2O$									
$[Ni(H_1HY)(H_1A)]$	3413	_	_	1599	_	1029	_		
$[Cu(H_1L)(H_1A)(NO_3) H_2O]NO_3$	3373	3188	1596	1550	1252	1094	_		
$[Cu(H_1N)(H_1A)(NO_3)_2]$	_	3120	1597	1520	1266	1036	_	1462	
$[Cu(H_1N)(en)(NO_3)_2]$	_	3332 3242 3125	1612	1578	1202	1081		1460	
$[Cu(H_1HY)_2 (en)]NO_3$	3327	3251 3283 3161	1600	1546	1266	1043			
$[Mn(H_1A)(en)(SO_4)(H_2O)]$	3404	3288	1664	1606	1259	1019			1076

The $n\rightarrow\pi^*$ transition was derived from the carbonyl group (C=O) and the Azomethine group (C=N) present in the ligands (Alhadi et al, 2012). The assignment of bands (d-d transitions) in Cu(II) complexes is complex due to low symmetry environment (less than cubic) in which the Cu(II) ion is found (Odunola et al., 2002). The spectrum of $[Cu(Phen)(H_1)](NO_3)H_2O$ in chloroform exhibited bands typical of square planar complex (Nishida & Kida, 1970) while $[Cu(Bipy)H_1L]NO_3$ and $Cu(Phen)H_1L]NO_3$ showed absorption bands in chloroform in the range 16,611-16,778 cm^{-1} which are consistent with square pyramidal geometry (Odunola et al., 2003). The electronic spectra of $[Cu(H_1L)(H_1A)(NO_3)H_2O]NO_3$ and $[Cu(H_1N)(H_1A)(NO_3)_2]$ displayed bands at 16,287 and 14,925 cm^{-1} respectively in chloroform assigned to octahedral geometry (Gudasi et al 2006) . Absorption bands at 20,964 cm^{-1} and 18,692 cm^{-1} have been assigned to distorted Octahedral in $[Cu(H_1HY)(H_1A)(NO_3)H_2O].(NO_3)2H_2O$. Solid reflectance spectra of $[Cu(H_1HY)(H_1A)(NO_3)H_2O]$, $[Cu(H_1N)(en)(NO_3)_2]$ and $[Cu(H_1HY)(en)(NO_3)_2]6H_2O$ showed absorption at 20,921-21,978cm^{-1} and 14,164-15,129cm^{-1} typical of distorted Octahedral geometry. $[Ni(Bipy)H_1LNO_3]$ and $[Ni(Phen)H_1L(NO_3)]$ have three absorption bands typical of octahedral geometry at 12,407-13,175, 18,182 and 22,321-24,938 assigned to $3A_{2g}(F) \rightarrow 3T_{2g}(F)$, $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ and $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ transitions respectively (Omoregie, 2018). This proposed geometry is backed up by the observed magnetic moment around 2.8-3.1 BM expected for Ni(II) with an Octahedral stereochemistry. However, the assignment of bands in the spectra of $[Ni(H_1HY)(H_1A)]$ is quite different. Here two bands were observed at 23,202 and 11,468cm^{-1} assigned to the $^1B_1g\leftarrow{}^1A_1g$ and $^1A_2g\leftarrow{}^1A_1g$ transitions respectively. This transitions are expected for square planar Ni(II) complexes (Jain and Mishra, 2012)

The solid reflectance spectra of $[Co(Bipy)(H_1L)_2]Cl_2$ and $[Co(Phen)(H_1L)_2]$ have bands at 11,765-12,165, 14,837-14,948, 20,921-22,422 which have to assigned to $^4T_{2g}\leftarrow{}^4T_{1g}$, $^4A_{2g}\leftarrow{}^4T_{1g}$ $^4T_{1g}(P)\leftarrow{}^4T_{1g}$ respectively.

These absorption patterns are consistent with six-coordinate, octahedral geometry (Shukla et al., 2008; Woods et al., 2004).

$[Mn(Bipy)(H_1L)_2]6H_2O$, $[Mn(Phen)(H_1L)_2]6H_2O$ and $[Mn(H_1A)(en)(SO_4)(H_2O)]$ displayed absorption bands typical of octahedral geometry(Greenwood and Earnshaw).

Table 3: Electronic Solution Spectra of mixed ligand Mn(II), Co(II), Ni(II) and Cu(II) complexes of some hydrazones and nitrogen donor ligands

Compound	Solvent	Band position (cm^{-1})	Tentative Assignment	Stereochemistry
H_1	Methanol	47,847 28,571	π→π* n→π*	
	Chloroform	31,056	π→π*	
H_1L	Chloroform	31,646 26,525 27,322	π→π* n→π* n→π*	
H_1A	Chloroform	31,250 29,586	π→π* n→π*	
$[Cu(Phen)(H_1)](NO_3)$	Chloroform	32,680 28,329 27,248 17,212 14,771	π→π* n→π* n→π* d-d	Square planar
$[Cu(Bipy)H_1L]NO_3$	Chloroform	47,847 28,571 22,321 16,611	π→π* n→π* C.T d-d	Square Pyramidal
$[Cu(Phen)H_1L]NO_3$	Chloroform	31,645 27,472 26,667 23,866 16,778	π→π* n→π* n→π* C.T. d-d	Square Pyramidal
$[Cu(H_1L)(H_1A)(NO_3)]$				Octahedral

$H_2O]NO_3$	Chloroform	31,250 26,110 24,938 23,641 16,287	π→π* n→π* C.T. C.T. $^2E_g \leftarrow {}^2T_{2g}$	
$[Cu(H_1N)(H_1A)(NO_3)_2]$	Chloroform	33,784 30,675 24,814 23,697 14,925	π→π* n→π* C.T. C.T. $^2E_g \leftarrow {}^2T_{2g}$	Octahedral
$[Cu(H_1HY)(H_1A)(NO_3)H_2O].(NO_3)2H_2O$	Chloroform	32,362 31,847 27,473 20,964 18,692	π→π* π→π* n→π }d-d	Distorted Octahedral

Table 4: Solid Reflectance Spectra of ligands, mixed ligand Mn(II), Co(II), Ni(II) and Cu(II) complexes of some hydrazones and nitrogen donor ligands

Compound	Band Position* (cm^{-1})	Tentative Assignment	Stereochemistry
H_1HY	40,486 34,364 31,847	π→π* π→π* π→π*	
H_1N	40,323 33,898 31,847	π→π* π→π* π→π*	
$[Ni(Bipy)H_1LNO_3]$	33,784 31,152 27,933 25,773 24,938 18,182 13,175	π→π* π→π* C.T. $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ $3A_{2g}(F) \rightarrow 3T_{2g}(F)$	Octahedral
$[Ni(Phen)H_1L(NO_3)]$	40,000 33,898	π→π* π→π*	

	31,348	$\pi \rightarrow \pi^*$	Octahedral
	28,329	$n \rightarrow \pi^*$	
	24,938	$3A_{2g}(F) \rightarrow 3T_{1g}(P)$	
	22,321	$3A_{2g}(F) \rightarrow 3T_{1g}(F)$	
	12,407	$3A_{2g}(F) \rightarrow 3T_{2g}(F)$	
$[Ni(H_1L)(en)(NO_3)].3H_2O$	33,784	$\pi \rightarrow \pi^*$	Octahedral
	31,152	$\pi \rightarrow \pi^*$	
	27,933	$n \rightarrow \pi^*$	
	25,773	C.T	
	24,938	$3A_{2g}(F) \rightarrow 3T_{1g}(P)$	
	18,182	$3A_{2g}(F) \rightarrow 3T_{1g}(F)$	
	13,175	$3A_{2g}(F) \rightarrow 3T_{2g}(F)$	
$[Co(Bipy)(H_1L)_2]Cl_2$	33,784	$\pi \rightarrow \pi^*$	Octahedral
	31,153	$\pi \rightarrow \pi^*$	
	27,933	$\pi \rightarrow \pi^*$	
	25,641	$n \rightarrow \pi^*$	
	24,938	C.T	
	22,422	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
	14,948	${}^4A_{2g} \leftarrow {}^4T_{1g}$	
	11,765	${}^4T_{2g} \leftarrow {}^4T_{1g}$	
$[Co(Phen)(H_1L)_2]$	39,841	$\pi \rightarrow \pi^*$	
	33,784	$\pi \rightarrow \pi^*$	
	31,847	$\pi \rightarrow \pi^*$	
	28,011	$n \rightarrow \pi^*$	
	22,989	C.T	
	20,921	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
	14,837	${}^4A_{2g} \leftarrow {}^4T_{1g}$	
	12,165	${}^4T_{2g} \leftarrow {}^4T_{1g}$	
$[Mn(Bipy)\ (H_1L)_2]6H_2O$	39,683	$\pi \rightarrow \pi^*$	Octahedral
	33,784	$\pi \rightarrow \pi^*$	
	31,447	$\pi \rightarrow \pi^*$	
	28,249	$n \rightarrow \pi^*$	
	23,095	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	
	19,194	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$	
$[Mn(Phen)\ (H_1L)_2]6H_2O$	39,683	$\pi \rightarrow \pi^*$	Octahedral
	31,847	$\pi \rightarrow \pi^*$	
	28,011	$n \rightarrow \pi^*$	
	21,552	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	
	14,948	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$	
$[Cu(H_1HY)(H_1A)(NO_3)H_2O]$	39,841	$\pi \rightarrow \pi^*$	

	33,784 31,847 28,409 20,921 14,815	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ }d-d	Distorted Octahedral
$[Ni(H_1HY)(H_1A)]$	40,161 33,784 31,348 28,329 23,202 11,468	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $^1B_1g\leftarrow{}^1A_1g$ $^1A_2g\leftarrow{}^1A_1g$	Square Planar
$[Cu(H_1N)(en)(NO_3)_2]$	39,841 33,898 31,847 21,692 15,129	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ }d-d	Distorted Octahedral
$[Cu(H_1HY)(en)(NO_3)_2]6H_2O$	39,841 33,784 30,488 23,148 21,978 14,164	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ C.T. }d-d	Distorted Octahedral
$[Mn(H_1A)(en)(SO_4)(H_2O)]$	39,841 33,784 31,847 28,169 24,938 20,576 19,455	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ C.T. $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ $^6A_{1g}\rightarrow{}^4T_{1g}(G)$	Octahedral

Antimicrobial Activities

The antimicrobial activities of mixed ligand nickel(II), cobalt(II) and copper(II) complexes of hydrazones were carried out and tested against six microbial organisms using agar diffusion method. $[Cu(H_1HY)(en)(NO_3)_2]6H_2O$, $[Cu(H_1HY)(H_1A)(NO_3)H_2O].(NO_3)2H_2O$, $[Cu(H_1L)(H_1A)(NO_3)H_2O]NO_3$, $[Co(Bipy)H_1L)_2]Cl_2$ and $[Cu(Phen)H_1L]NO_3$ showed pronounced activity on the tested bacterial strains except $[Cu(H_1HY)(H_1A)(NO_3)H_2O].(NO_3)2H_2O$ and $[Cu(H_1HY)(en)(NO_3)_2]6H_2O$ in Staphylococcus aureus and *Pseudomonas aeruginosa* that showed moderate activity. $[Cu(H_1N)(H_1A)(NO_3)_2]$ and $[Ni(H_1L)(en)(NO_3)].3H_2O$ lacked antibacterial activity except $[Cu(H_1N)(H_1A)(NO_3)_2]$ in *Penicillium notatum* with pronounced activity. All the complexes showed pronounced activity on the tested fungi (*Candida albicans and Aspergillus niger*) except $[Cu(H_1N)(H_1A)(NO_3)_2]$ and $Ni(H_1L)(en)(NO_3)].3H_2O$ that lacked fungi activity. The complexes compared favourably well with the Gentamicin and Ketoconazole used with respect to antibacterial and antifungal activities respectively.

Table 5: Antimicrobial Activities of of mixed ligand Mn(II), Co(II), Ni(II) and Cu(II) complexes of some hydrazones and nitrogen donor ligands

Compound	**E. coli**	**S. aur**	**P. aer**	**Pen**	**Ca**	**An**
$[Cu(H_1HY)(en)\ (NO_3)_2]6H_2O$	23	20	16	30	31	29
$[Cu(H_1N)\ (H_1A)(NO_3)_2]$	R	R	R	27	R	R
$[Cu(H_1HY)\ (H_1A)(NO_3)\ H_2O].\ (NO_3)2H_2O$	21	19	20	29	30	27
$[Cu(H_1L)\ (H_1A)(NO_3)\ H_2O]NO_3$	26	20	20	31	31	28
$[Co(Bipy)\ (H_1L)_2]Cl_2$	25	27	23	24	22	23
$[Cu(Phen)(H_1)](NO_3)H_2O$	27	26	27	24	21	25
$[Ni(H_1L)(en)\ (NO_3)].3H_2O$	R	R	R	R	R	R
$[Cu(Phen)H_1L]\ NO_3$	28	25	24	27	23	30
Gentamycin/Ketoconazole	20	20	20	30	30	26
Methanol	No activities					

S. aur = Staphylococcus aureus ; E. coli = Escherichia coli; P. aer = Pseudomonas aeruginosa; Pen =Penicillium notatum; Ca = Candida albicans; An = Aspergillus niger; Pen =Penicillium notatum

CONCLUSION

The hydrazide, hydrazones and their metal complexes were synthesized using the procedures provided in literature but with a little modification. The molar conductance of $[Cu(Phen)(H_1)](NO_3)H_2O]$, $[Cu(Bipy)H_1L]NO_3$, $[Cu(Phen)H_1L]NO_3$, $[Cu(H_1HY)(H_1A)(NO_3)H_2O].(NO_3)2H_2O$ and $[Cu(H_1L)(H_1A)(NO_3)H_2O]NO_3$ in nitromethane shows that these complexes are 1:1 electrolytes while $[Co(Bipy)(H_1L)_2]Cl_2$ is a 1:2 electrolyte. The infrared spectra of the ligands and the mixed ligand complexes reveal that there is coordination between the ligands and the metals and the absence of the v(C=O) and v(NH) bands in some complexes shows that tautomerism has taken place. The Cu(II) complexes have octahedral or distorted octahedral geometry except $[Cu(Bipy)H_1L]NO_3$ and $Cu(Phen)H_1L]NO_3$ with square pyramidal geometry, also octahedral geometry was proposed for all the Ni(II) complexes except $[Ni(H_1HY)(H_1A)]$ with a square planar geometry. However, all the Co(II) and Mn(II) complexes have Octahedral stereochemistry.

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