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Synthesis, Characterization and Antimicrobial Activity Study of metal (II) Complexes of Mixed Acetylsalicylic acid and 1, 10- phenanthroline

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Abstract
A series of Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) mixed ligands-metal complexes derived from 1,10-phenanthroline (PHEN) and acetylsalicylic acid (ASP) have been synthesized. The compounds were characterized using elemental analysis, infrared, ultraviolet/visible spectroscopies and X-ray powder diffraction .The coordination of the two ligands towards the central metal ion has been proposed in the light of elemental analysis, infrared, ultraviolet/ visible, and X-ray powder diffraction spectroscopic studies. The results of the physical and spectroscopic data confirmed that the ligands are bidentate chelating agents. In 1, 10-phenanthroline, coordination occurred through the two pyridinic nitrogen groups. Acetylsalicylic acid complexes coordinate through the carbonyl oxygen of the carboxyl and the ester groups. The compounds form a six- coordinate geometry. Antimicrobial activity of the mixed ligand metal complexes and the free ligands were carried out against the bacteria: *Escherichia coli, staphylococcus aureus, klebsiella pneumonia, pseudomonas aeruginosa* and the fungi *candida spp*. The mixed ligands metal complexes showed higher activities when compared to the free ligands of acetylsalicylic acid but were less active than the free 1, 10-phenanthroline ligand. The complexes of Mn (II) showed significant antimicrobial activity while the Fe (II) complex exhibited the least activity against the bacteria and fungi organisms.

Keywords: 1, 10-phenanthroline, aspirin, complexes, transition metal, spectroscopy, antimicrobial.

1. Introduction

Coordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound. On the basis of nature of the metal as well as the type of ligand, these metal complexes have extensive applications in various fields of human interest (Johari *et al.*, 2009; Mittal and Uma 2010). Chelation or complexation shows more potent antibacterial effect against some microorganisms than the respective drugs (Kesharwani and Singh 2010; Habib *et al*., 2011). The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of metals in living organisms (Bajpai *et al.*, 1982; Sullivan *et al.*, 1979).

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Nitrogen containing chiral ligands have found wide applications in chemotherapy and asymmetric catalysis. Among them 1, 10 – phenanthroline is particularly attractive for its ability to coordinate several metal ions, and thus to generate different catalytic species involved in a great variety of reactions (Puglisi *et al.*, 2003). The ligand 1, 10 – phenanthroline is a strong field bidentate ligand that form very stable chelates with many first row transition metals (Lee, 1991). Aspirin is a derivative of salicylic acid, it has analgesic, anti-inflammatory and antipyretic actions and inhibits prostaglandrin synthetase (British Pharmaceutical Codex, 1977).

A lot of metal complexes of 1, 10-phenanthroline and aspirin have been reported in combination with other ligands (Mohamed *et al.*, 2014; Dhanalakshmi, 2013; Agwara, *et al*., 2013; Adeoye *et al.*, 2013; Hossain, 2013; Lawal and Obaleye, 2007). However, very few reports have appeared in literature for the mixed ligands-metal complexes of 1, 10-phenanthroline and aspirin. Thus, this article reports the synthesis, characterization and antimicrobial activity of some mixed metal complexes of 1, 10-phenanthroline with acetylsalicylic acid.

2. Materials and Methods

Metal salts used for this synthesis were obtained from British Drug House Chemical Limited (BDH), England and were used as supplied. 1, 10-Phenanthroline was obtained from KEM Light laboratories PVT. LTD, India and aspirin used was sourced from Emzor Pharmaceuticals, Lagos. Cultures of the micro-organisms used were obtained from Department of Microbiology, University of Ilorin. Ilorin. Nigeria.

Synthesis of mixed ligands-metal complexes

The method described by Agwara *et al*. (2010) was employed in the synthesis of the mixed ligand-metal complexes of 1, 10-phenanthroline with acetylsalicylic acid. 1 mmol of each of the metal salts ($MnCl_2.4H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $FeCl_2.4H_2O$ and $ZnCl_2$) was dissolved in 10 ml of appropriate solvent and stirred at room temperature. 2 mmol each of the ligands 1, 10-phenanthroline (PHEN) (0.396 g) and acetylsalicylic acid (ASP) (0.360 g) was dissolved in 10 ml of ethanol and added in drops to the stirred metal salt solution at room temperature. After the addition of the ligands in drops, the solution was further stirred for one hour. The colour change and pH were recorded. The solution obtained was left standing undisturbed for slow evaporation for 10-17 days. The crystals / powder formed were washed

with a mixture of ethanol and distilled water and dried in a desiccator over silica gel. The proposed equation for the reaction:

$$MX_2.nH_2O + ASP + PHEN \longrightarrow [M(ASP)(PHEN)(H_2O)_2]X_2,$$

M = metal ion, X = Halide, ASP = acetylsalicylic acid, PHEN = 1, 10-phenanthroline.

Characterization of the complexes

The infrared spectra of the ligands and complexes were recorded in KBr pellet in the range (400 – 4000 cm^{-1}) on IR Affinity-1S FT-IR spectrophotometer. The electronic spectra were recorded on Aquamate scientific spectrophotometer model V 4.60. The elemental analyses were recorded on Perkin-Elmer CHN Analyzer 2400 series II. Conductivity measurements were carried out on Hanna EC 214 conductivity meter with a cell constant of 0.83. Powder XRD analysis was measured on a Bruker D8 Advance X-ray diffractometer.

Antimicrobial studies:

The antimicrobial activities of the free ligands and the mixed ligand-metal complexes was carried out according to the method described by Adediji *et al.* (2009). The bacterial species used for this study include *Escherichia Coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Klebsiella spp*., and the fungi *Candida spp*.

3. Results and Discussion

The results of the physical properties of the ligands and their complexes are presented in table 1.

Table 1: Some physical properties of 1, 10-phenanthroline, Acetylsalicylic acid and their complexes.

Ligands/ complexes	**State**	**Colour**	**Melting point (^{0}C)**	**Conductivity (μScm^2)**
1,10-phenanthroline	Crystalline	White	117	
Acetylsalicylic acid (ASP)	Powdery	White	158.6	
$[Mn(ASP)(PHEN)(H_2O)_2]Cl_2$	Crystalline	Yellow	248–250	16.4
$[Cu(ASP)(PHEN)(H_2O)_2]Cl_2$	Crystalline	Green	150 – 152	57.8
$[Co(ASP)(PHEN)(H_2O)_2]Cl_2$	Crystalline	Red	238(decompose)	36
$[Fe(ASP)(PHEN)(H_2O)_2]Cl_2$	Powdery	Red	350 – 352	52.6
$[Zn(ASP)(PHEN)(H_2O)_2]Cl_2$	Powdery	Pink	300(decompose)	5.8

The results of the elemental analysis of some of the complexes are presented in table 2 below.

Table 2: The results of the elemental analysis

Complexes	**% Calculated (% Found)**			
	% C	**% H**	**% N**	**% O**
$[Mn(ASP)(PHEN)(H_2O)_2]Cl_2$	48.28 (48.51)	3.82 (4.04)	5.36 (5.51)	18.39 (18.77)
$[Cu(ASP)(PHEN)(H_2O)_2]Cl_2$	47.50 (47.53)	3.77 (3.77)	5.28 (5.34)	18.10 (18.11)

The result of elemental analysis results for carbon, hydrogen, nitrogen and oxygen found were very close to the calculated values which is an indication of the purity of the complexes and also indicated that the ligands coordinated to the central metal ion in the ratio 1:1:1 . The results of the conductivity data showed that the complexes behave as electrolytes in solution, which is in agreement with that of Adediji *et al*. (2009).

The results of the electronic spectra of the ligands and their complexes are presented in table 3 below.

Table 3: The electronic Spectra for the free ligands and its complexes.

LIGANDS / COMPLEXES	WAVELENGTH (nm)	ENERGIES (cm^{-1})	TENTATIVE ASSIGNMENT
1,10-phenanthroline	331	30211	$n \rightarrow \pi^*$
Acetylsalicylic acid (ASP)	328	30488	$n \rightarrow \pi^*$
$[Mn(ASP)(PHEN)(H_2O)_2].Cl_2$	320	31250	MLCT
	331	30211	MLCT
$[Co(ASP)(PHEN)(H_2O)_2].Cl_2$	329	30395	MLCT
	360	27778	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$
$[Fe(ASP)(PHEN)(H_2O)_2].Cl_2$	448	22321	MLCT
	529	18904	$^5T_{2g} \rightarrow {}^5E_g$,
$[Cu(ASP)(PHEN)(H_2O)_2].Cl_2$	327	30581	MLCT
$[Zn(ASP)(PHEN)(H_2O)_2].Cl_2$	297	33670	$n \rightarrow \pi^*$

The electronic spectra data of the ligands and its mixed complexes**,** were recorded at room temperature in dimethylsulfoxide (DMSO) solution at 200-800 nm**.** The absorption bands observed at 328 nm (Acetylsalicylic acid) and 331 nm (1, 10-Phenantholine) were assigned to $n \rightarrow \pi^*$ transition, as a result of intra ligand charge transfer (ILCT) of the aromatic chromophores (Lever, 1968). The $[Co(ASP)(PHEN)(H_2O)_2].Cl_2$ complex show bands at 360 and 329 nm, assignable to transitions of $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ and Metal ligand charge transfer (MLCT respectively, which is a characteristic of an octahedral complex ((Lever,1968). The band of 327 nm for $[Cu(ASP)(PHEN)Cl_2](H_2O)_2].Cl_2$ and (320, 331 nm) for $[Mn(ASP)(PHEN)(H_2O)_2].Cl_2$ complexes were assigned to MLCT transitions. Also, The band of 311 nm for $[Mn\ (SA)(PHEN)(H_2O)_2].Cl_2$ and (320, 331 nm) for $[Mn(ASP)(PHEN)(H_2O)_2].Cl_2$ were assigned to MLCT transitions. These bands are forbidden and diffused, due to its d^5 configuration, electrons occupying both lower and upper orbitals (Lever,1968).The $[Fe(ASP)(PHEN)(H_2O)_2].Cl_2$ show bands at 448 and 529 nm, assignable to MLCT and $^5T_{2g} \rightarrow {}^5E_g$, which are features of octahedral geometry (William, 1991).

A band of 557 nm was observed for the $[Fe\ (SA)(PHEN)(H_2O)_2].Cl_2$ complex, with probable assignment of $^5T_{2g} \rightarrow {}^5E_g$. The $[Cd(SA)(PHEN)(H_2O)_2].Cl_2$ complex display bands at 327 nm, as a result of possible charge transfer of the metal to ligand. An octahedral geometry was however proposed (Singh, 2010). Bands due to $[Hg(SA)(PHEN)(H_2O)_2].Cl_2$ and [Hg(ASP)

(PHEN) $(H_2O)_2].Cl_2$ complexes were observed in a range of 325-693 nm and assigned to transitions of MLCT [60]. The $[Zn(ASP)(PHEN)(H_2O)_2].Cl_2$ and $[Zn(SA)(PHEN)(H_2O)_2].Cl_2$ complexes display new bands at 297 and 299 nm respectively, due to intra-ligand charge transfer and the ground term symbol shows no splitting with a d^{10} configuration and completely filled d-orbitals. Due to the weak absorption bands intensity, an octahedral geometry was proposed with possible assignments of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. Results of selected infrared spectra of 1, 10-phenanthroline (PHEN), aspirin (ASP), and their metal complexes are presented in table 4 below

Table 4: The characteristic infrared data (cm^{-1}) of 1, 10-phenanthroline, aspirin (ASP), their metal complexes**.**

LIGANDS/ COMPLEXES	*ν*(C=N)	*ν*(C=O) ester	*ν*(C=O) acid	*ν*(C-O) acid	*ν*(C-O) ester	ν(O-H) acid	*ν*(M-O=C)	*ν*(M-OH)	*ν*(M-N)
1,10-phenanthroline	1630br								
Acetylsalicylic acid (ASP)	__	1761 br	1680 br	1213 w	1288 w	3491 m			
$[Mn(ASP)(PHEN)(H_2O)_2].Cl_2$	1512.1 w	-------	--------	1250 w	1028. m	3061 m	665.44 s	540 s	466.7 s
$[Cu(ASP)(PHEN)(H_2O)_2].Cl_2$	1512.0 5	_____ _	1627 w	1222 m	1103 m	3055. 24	646.15 m	524 sh	426.27 m
$[Co(ASP)(PHEN)(H_2O)_2].Cl_2$	1514.1 2s	1757 s	1627 s	1267 m	1012 m	3385 br	638.44 m	536.21 m	420.48 sh
$[Zn(ASP)(PHEN)(H_2O)_2].Cl_2$	1506 br	1780.3 w	1605 w	____	1116 br	3394 br	1614.3 5 w	503.44 w	456.18 w
$[Fe(ASP)(PHEN)(H_2O)_2].Cl_2$	___	1431.2 w	1643.3 w	_____	1143 m	3408b r	689.57 w	517.27 w	396.34 m

The assignments have been carried out based on comparison of the spectra data with those of similar compounds (William, 1991). The absorption band at 3491.3 cm^{-1} in the spectrum of free aspirin has been attributed to O-H group. This band undergo hypsochromic shift to between 3385.07 cm^{-1} and 3045.5 cm^{-1} in the metal complexes. The shifting of these (O-H) stretching vibrational band provide evidence that this group is one of the coordination sites of Aspirin. The bands at 1761 cm^{-1} and 1680 cm^{-1} have been assigned to C=O of ester and carboxylic acid respectively, these bands also undergo hypsochromic shift in the spectra of the complexes. The shifting of these (C=O) stretching bands provides evidence that this

group is also one of the coordination sites of Aspirin. The strong absorption band at 1213 cm^{-1} have been attributed to C-O stretching vibration of the carboxylic acid while the medium bands at 1288 cm^{-1} have been attributed to C-O stretching vibration of the ester. While from the spectrum of the free 1, 10-phenanthroline the band at 1630 cm^{-1} has been assigned to the C=N group in the free ligand, this band of the C=N group also undergo hypsochromic shift between 1630-1508 cm^{-1} which is also an evidence that this group is also a coordination site for 1, 10-phanthroline. The strong absorption bands between the ranges of 632 cm^{-1}- 651 cm^{-1} and 416 cm^{-1} – 466 cm^{-1} on the spectra of the metal complexes which could not be traced to free acetylsalicylic acid and 1,1-phenanthroline have been tentatively assigned to [M-OH], [M-O=C] and [M-N] (Nakamato, 1970). In addition, the bands of coordinated water observed at the range of 842 cm^{-1} -869 cm^{-1} support the proof that there is the presence of water in the lattice of the complexes (Mahmoud *et at*., 2013; El-Ghamry, 2013; Shebl, 2011).

The powder X-ray diffraction pattern for the ligands; 1, 1-phenanthroline and aspirin, and some of the mixed ligands metal complexes is reported in figure 1. The X- ray diffraction data were recorded by using Cu Kα radiation (1.5406 Angstrom). The PXRD patterns of ligand and mixed complexes were collected over a 2θ range of 10-40° as shown in Fig.1. XRD patterns ligands differ to that of the mixed complexes with different (2-theta) values, indicate complexation ((Dhanaraj and Nair, 2009). The mixed complexes sharp crystalline peaks indicating their crystalline phase (Dhanaraj and Nair, 2009).

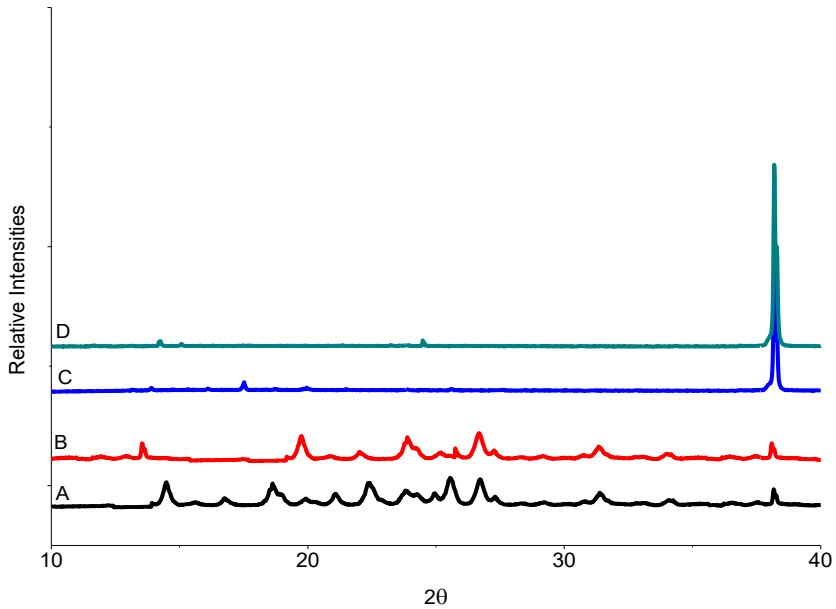


Fig 1: The powder X-ray diffraction pattern of the ligands and the complexes. Where A =Aspirin, B= 1,10-phenanthroline, C=**[**Mn(ASP)(PHEN)(H_2O)].Cl_2 , D= [Cu (ASP)(PHEN)(H_2O)].Cl_2 .

On the basis of the analytical data obtained such as melting point, solubility test, conductance, elemental analysis and the spectroscopic data from UV-Visible, IR, and PXRD the following octahedral geometry structure has been proposed for the new complexes. (Fig.

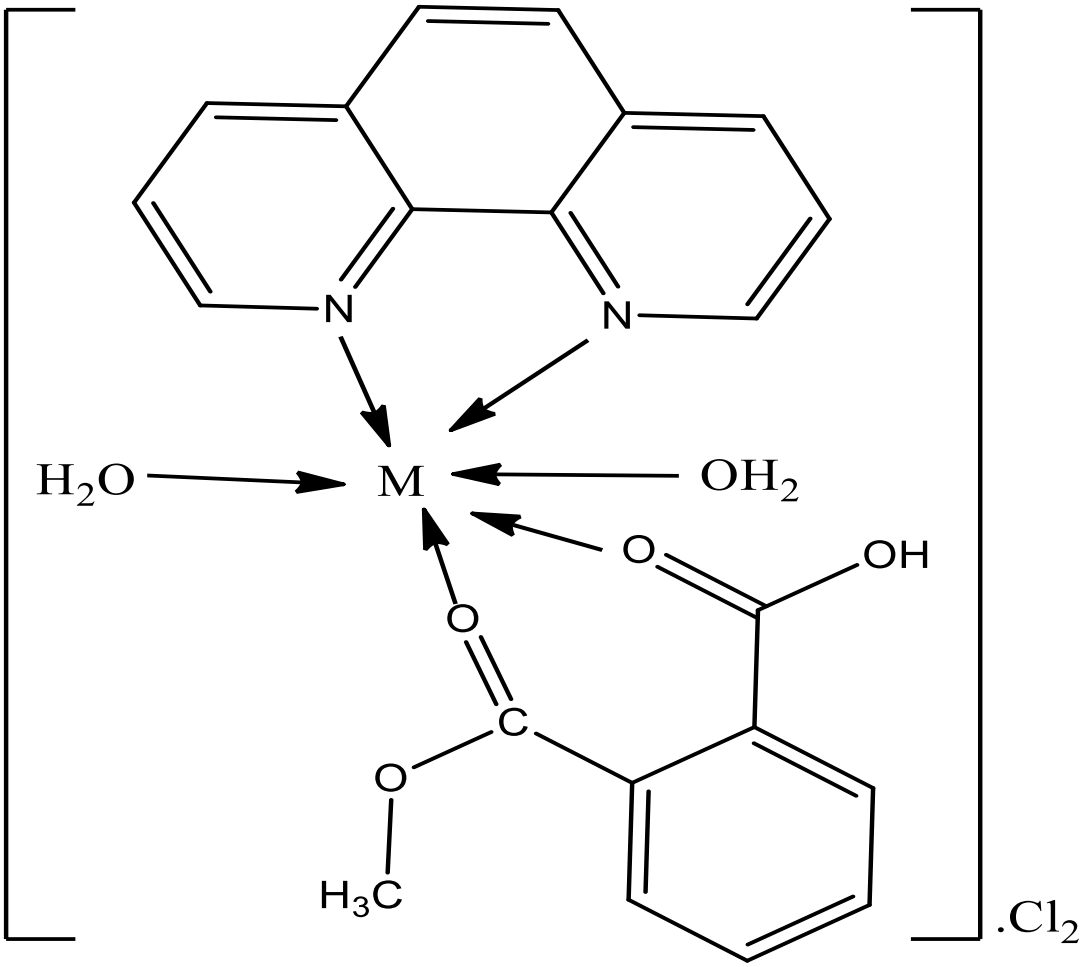
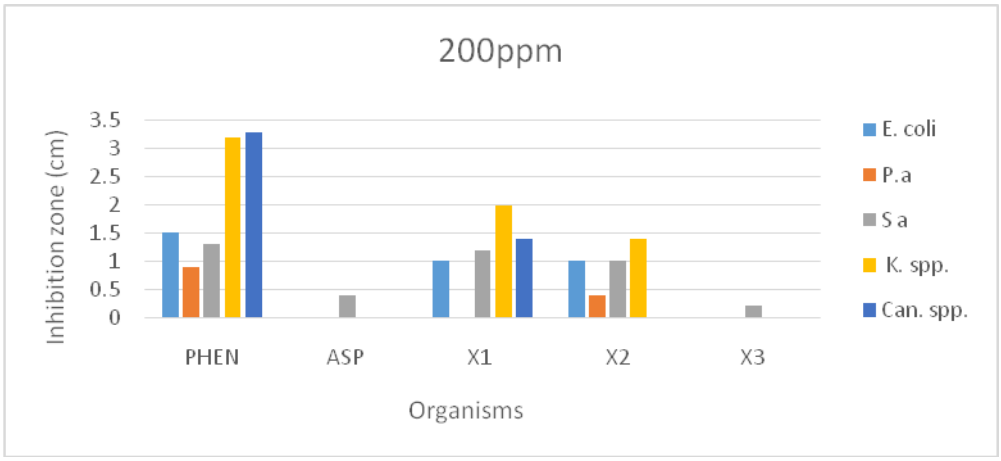


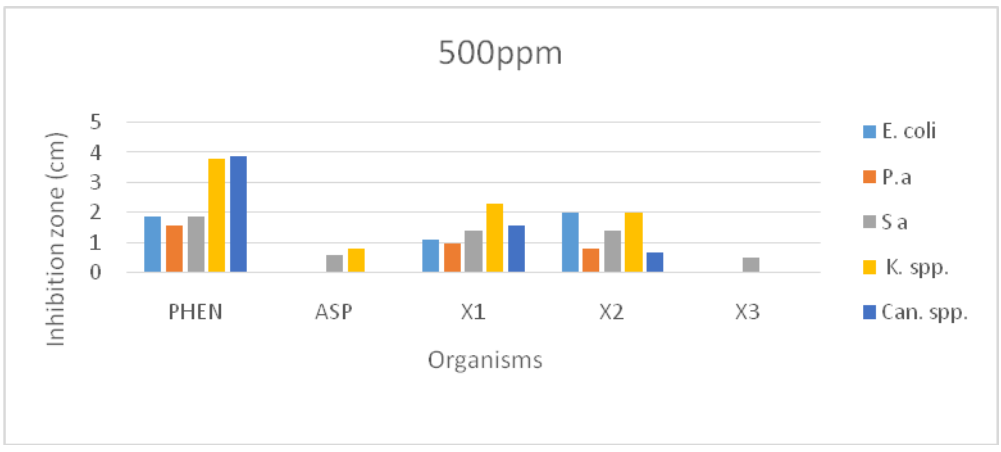
Fig 2: Proposed Structure of the $[M(ASP)(PHEN)(H_20)_2]Cl_2$, where M = Mn(II), Cu(II), Fe(II), Co(II), Zn(II)**.**

Antimicrobial activity studies of the free ligands and some their complexes are presented in table 5 below.

Table 5: Comparison of the antimicrobial activity of the free ligands and some of their complexes.

Ligands/complexes	***Escherichia Coli***		***Pseudomonas.a***		***Staphylococcus.a***		***Klebsiella* spp.**		***Candida.* spp.**	
	Concentration of ligands and mixed complexes (ppm)									
	200	500	200	500	200	500	200	500	200	500
1,10-phenanthroline	1.5	1.9	0.9	1.6	1.3	1.9	3.2	3.8	3.3	**3.9**
Acetylsalicylic acid (ASP)	0	0	0	0	0.4	0.6	0	0.8	0	**0**
[Mn(ASP)(PHEN)(H_2O)]. Cl_2	1.0	1.1	0	1.0	1.2	1.4	2.0	2.3	1.4	**1.6**
[Cu(ASP)(PHEN)(H_2O)]. Cl_2	1.0	2.0	0.4	0.8	1.0	1.4	1.4	2.0	0	**0.7**
[Fe(ASP)(PHEN)(H_2O)]. Cl_2	0	0	0	0	0.2	0.5	0	0	0	**0**





where; PHEN = 1,10-phenanthroline, Asp = Acetylsalicylic acid
X1= $[Mn(ASP)(PHEN)(H_2O)].Cl_2$
X2= $[Cu(ASP)(PHEN)(H_2O)].Cl_2$
X3= $[Fe(ASP)(PHEN)(H_2O)].Cl_2$

The results of the antimicrobial activity of the free ligands compared to their mixed complexes showed that the free 1,10-Phenanthroline is most active against the five organisms; *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Klebsiella spp*. and *Candida spp*. on which the tests were carried out has compared to the free aspirin ligand that showed minute activity against the organisms (Agwara, 2010).

The mixed ligand-metal complexes showed improved antimicrobial activity mainly due to the presence of the metal which coordinates the individual ligands together (Agwara 2012). The complexes showed identical activities when both concentrations (200 ppm and 500 ppm) used for the test were compared which is an indication that the activity of the complexes is not solely dependent on the concentration of the solution but also on the inherent activity of the complexes. The $[Mn(ASP)(PHEN)(H_2O)_2].Cl_2$ showed the most activity while $[Fe(ASP)(PHEN)(H_2O)_2].Cl_2$ showed the least activity of all the complexes.

4. Conclusion

Some Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) mixed complexes of 1,10-phenanthroline (PHEN) and acetylsalicylic acid (ASP) have been synthesized and characterized using elemental analysis ,infrared, ultraviolet/visible spectroscopies and X-ray powder diffraction .The coordination of the two ligands toward the central metal ion has been proposed in the light of elemental analysis, X-ray powder diffraction and spectroscopic studies. The results of the physical and spectroscopic data confirmed that the ligands are bidentate chelating agents, forming complexes with six- coordinate geometry. Antimicrobial activity of the mixed ligand metal complexes and the free ligand were carried out against the bacteria: *Escherichia coli, staphylococcus aureus, klebsiella pneumonia, pseudomonas aeruginosa* and the fungi *candida species*. The mixed ligand metal complexes showed higher activities when compared to the free ligands of acetylsalicylic acid but were less active than the free 1, 10-phenanthroline ligand.

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