



## Synthesis, Characterization and Antimicrobial Activity of Mixed Transition Metal Complexes of Salicylic Acid with 1, 10-Phenanthroline

<sup>\*1</sup> AMUDAT LAWAL; <sup>2</sup> ADEOLU S. SHODEINDE; <sup>3</sup> SALIU A. AMOLEGBE;  
<sup>1</sup> SUNDAY E. ELAIGWU; <sup>4</sup> MUSLIMAT T. YUNUS-ISSA

<sup>1</sup>Department of Chemistry, University of Ilorin, Ilorin, Kwara State, Nigeria

<sup>2</sup>Department of Industrial Chemistry, University of Ilorin, Ilorin, Kwara State, Nigeria

<sup>3</sup>Department of Chemistry, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria

<sup>4</sup>School of Science, Federal College of Education, Osiele, Abeokuta, Ogun State, Nigeria.

\*Correspondence author: [amudat1112@gmail.com](mailto:amudat1112@gmail.com) Tel +2348035850696

**ABSTRACT:** A new series of Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) mixed ligands-metal complexes derived from salicylic acid (SA) and 1,10-phenanthroline (PHEN) have been synthesized and characterized by spectroscopic studies. The coordination of the two ligands towards central metal ions has been proposed in the light of elemental analysis, IR, UV-vis spectroscopic studies. The results of the physical and spectroscopic data confirmed that the ligands are chelating agents. In 1, 10-phenanthroline, coordination occurred through the two pyridinic nitrogen groups, while in the salicylic acid coordination occurred through the oxygen of the hydroxyl and the carboxylic groups. All the complexes synthesized were of octahedral geometry. Antimicrobial activity of the mixed ligands metal complexes and the free ligands were carried out against the bacterial *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 salicylic acid but were less active than the free 1,10-phenanthroline ligand. The complexes of Cu (II) showed the highest antimicrobial activity while the Fe(II) complex showed the least activity against the bacterial and fungi organisms. © JASEM

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**Key Words:** 1,10-phenanthroline, Salicylic acid, Mixed ligands-metal complexes, Transition metal, Spectroscopy, Antimicrobial.

Transition metal complexes are cationic, neutral or anionic species in which a transition metal is coordinated by ligands (Cox, 2005). Transition metal ions are known to play very important roles in biological processes in the human body. For example, Zn (II) and Cu (II) ions are the second and third most abundant transition metals in humans (Kaim, *et al.*, (1996) and Xiao-Ming, *et al.*, (1996). They are found either at the active sites or as structural components of a good number of enzymes. Cobalt is present in vitamin B12, a co-enzyme that plays significant roles in some biochemical processes. There are numerous lists of transition metals which are effective therapeutic agents especially when coordinated to a ligand to form metal complexes. A list of metal containing compounds used in chemotherapy for treatment of diseases include platinum (anticancer), silver (antimicrobial), gold (antiarthritic), bismuth (antiulcer), antimony (antiprotozoal), vanadium (antidiabetic) and iron (antimalaria) (Huang, *et al.* (2005). 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 forms very stable chelates with many first row transition metals (Lee, (1991). Salicylic acid is biosynthesized from the amino acid phenylalanine and can be produced by sodium salicylate (Diarmiud, (2005) and Philip, (2000). In modern medicine, salicylic acid and its derivatives are used as constituents of some rubefacient products, for example, methyl salicylate is used as a liniment to soothe joint and muscle pain, choline salicylate is used typically to relieve the pain of aphthous ulcers (Wecker and Laubert, (2000).

A lot of metal complexes of 1,10-phenanthroline, salicylic acid have been reported in combination with other ligands, very few reports have appeared in literatures for the mixed ligands-metal complexes of 1,10-phenanthroline and salicylic acid. Thus, this article reports the synthesis, characterization and

antimicrobial activity of some mixed metal complexes of 1,10-phenanthroline and salicylic acid.

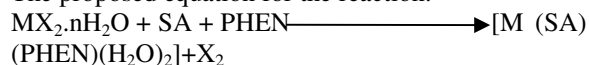
## MATERIALS AND METHOD

Metal salts used for these syntheses 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 salicylic acid used was sourced from Emzor Pharmaceuticals, Lagos. Cultures of the micro-organisms used were obtained from Department of Microbiology, University of Ilorin.

**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 salicylic acid. The metal salt 1 mmol (M=  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{ZnCl}_2$ ) were 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 salicylic acid (SA) (0.276 g) were dissolved in 10 ml of ethanol and added in drops to the already stirring 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 kept in a beaker covered with perforated aluminum foil in a quiet out of the way location for 21 days for the

evaporation of the solvent. The crystals 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:



M = metal ion, X = Halide, SA = salicylic acid, PHEN = 1,10-phenanthroline

**Characterization of the complexes:** The infrared spectra of the ligands and complexes were recorded in KBr pellets in the range ( $400 - 400 \text{ cm}^{-1}$ ) on IR Affinity-1S FT-IR spectrophotometer. The electronic spectra were recorded on Aquamate scientific spectrophotometer model V 4.60. The elemental analysis was recorded on Perkin-Elmer CHN Analyzer 2400 series II. Conductivity measurements were carried out HNNA EC 214 conductivity meter with a cell constant of 0.83.

**Antimicrobial studies:** The antimicrobial activities of the free ligands and the mixed ligand-metal complexes were determined according to the method described by Adediji *et al.*, (2009). The bacterial species used for this study are *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Klebsiella spp.*, and the fungi *Candida spp.*

## 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, salicylic acid and their complexes

Ligands/ complexes	State	Colour	Mpt ( $^{\circ}\text{C}$ )	Conductivity ( $\mu\text{Scm}^{-1}$ )
1,10-phenanthroline	Crystalline	White	117	
Salicylic acid	Powdery	White	158.6	
$[\text{Mn}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	Crystalline	Yellow	248–250	16.6
$[\text{Cu}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	Crystalline	Green	150 – 152	57.8
$[\text{Co}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	Crystalline	Red	238(decompose)	36
$[\text{Fe}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	Powdery	Red	350 – 352	52.6
$[\text{Zn}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	Powdery	Pink	300(decompose)	5.8

The complexes were only soluble in dimethyl sulfoxide except for  $[\text{Cu}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$  which was slightly soluble in hot distilled water and ethanol. The complexes melt above  $248^{\circ}\text{C}$ , with the exception of  $[\text{Cu}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$  which melts at  $152^{\circ}\text{C}$  and the complexes of  $[\text{Co}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$  and  $[\text{Zn}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$  which decomposed at 238 and  $300^{\circ}\text{C}$  respectively. (Mohamed *et al.*, (2014)

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(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	47.61 (47.64)	3.55 (3.56)	5.85 (5.85)	16.70 (16.72)
[Cu(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	46.77 (46.80)	3.49 (3.51)	5.74 (5.76)	16.41 (16.43)
[Fe(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	47.63 (47.65)	3.37 (3.38)	5.85 (5.87)	16.71 (16.73)

The elemental analysis results for carbon, hydrogen, nitrogen and oxygen found were very close to the calculated values which are an indication of the purity of the complexes and these also indicated that the ligands coordinated to the central metal ion in the ratio 1:1:1 that is L<sub>1</sub>-M-L<sub>2</sub>. Where L<sub>1</sub> = Ligand M = Metal salts and L<sub>2</sub> = Ligand.

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

**Table3:** The electronic Spectra for the free ligands and its complexes.

Ligands / complexes	Wavelength (nm)	Energies (cm <sup>-1</sup> )	Tentative assignment
1,10-phenanthroline	331	30211	n → π*
Salicylic Acid	317	31546	n → π*
[Mn(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	311	32154	MLCT
[Cu(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	360	27778	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>
[Co(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	312	32051	MLCT
[Fe(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	557	17953	<sup>5</sup> T <sub>2g</sub> → <sup>5</sup> E <sub>g2</sub>
[Zn(SA)(PHEN)(H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub>	299	33444	n → π*

The electronic spectra data of the ligands and its mixed complexes, which were recorded at room temperature in dimethyl sulfoxide (DMSO) solution at (200-800 nm). Broad absorption bands were observed at 317 nm (Salicylic acid), and 331 nm (1,10-Phenanthroline) and assigned to transitions of (n → π\*) as a result of intra ligand charge transfer (ILCT) of the aromatic chromophore (Lever, (1968). Band of 312 nm was observed in [Co(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> complex and assigned to transition of MLCT, which is a feature in octahedral stereochemistry. The [Cu(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> complex show band 360 nm and assigned to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> transition. The band of 311 nm for [Mn(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> is assigned to MLCT transitions, this band is forbidden and diffused due to :

its d<sup>5</sup> configuration, electrons occupying both lower and upper orbitals (Lever, (1968). The [Fe(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> shows band at 557nm, assignable to <sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub>, which is also a feature of octahedral geometry (William, 1991). [Zn(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> complexes displayed band at 299 nm, due to intra-ligand charge transfer and the ground term symbol shows no splitting with a d<sup>10</sup> configuration and completely filled d-orbitals. Due to the weak absorption bands intensity, an octahedral geometry was proposed with possible assignment of n → π\*.

Results of selected infrared spectra of 1,10-phenanthroline, salicylic acid (SA), and their metal complexes are presented in table 4 below

**Table 4:** The characteristic infrared data ( $\text{cm}^{-1}$ ) of 1,10-phenanthroline, salicylic acid (SA), their metal complexes.

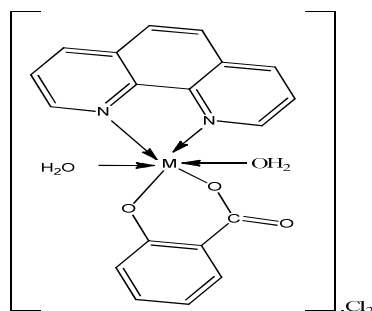
Ligands/Complexes	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{OCO})_{\text{asym}}$	$\nu(\text{OCO})_{\text{sym}}$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Salicylic acid	—	3421	1691	1460		
1,10-phenanthroline	1630	—				
$[\text{Mn}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	—	3059	1664	1487	468	542
$[\text{Cu}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	1606	3059	1664	1425	426	534
$[\text{Co}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	1514	3051	1656	1423	422	536
$[\text{Fe}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	—	3406	1644	1419	451	539
$[\text{Zn}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$	1499	3406	1640	1427	401	615

In order to get further information about the coordination behavior of the ligand salicylic acid (SA) and 1,10-phenanthroline (phen) with metal ions, comparison of the infrared spectra of the free ligands and their complexes were made. The broad band at  $3421\text{cm}^{-1}$  in the spectrum of the free ligand (SA) was assigned to the  $\nu(\text{O}-\text{H})$  group, while another strong absorption band at  $1691\text{cm}^{-1}$  could be explained as  $\nu(\text{OCO})_{\text{asym}}$  where the  $\nu(\text{OCO})_{\text{sym}}$  was noticed at  $1460\text{cm}^{-1}$  (Sliverstein *et al.*, (2005). The spectrum of free 1,10-phenanthroline (phen) showed band that was observed at  $1630\text{cm}^{-1}$  assigned to  $\nu(\text{C}=\text{N})$  (Greenwood *et al.*, (2011). The spectra of the complexes exhibited marked differences in the absorption band belonging to the stretching vibration of  $\nu(\text{O}-\text{H})$  of hydroxyl group which has been found in the range of  $3051 - 3361.93\text{cm}^{-1}$  to undergo a hypsochromic shift suggesting the possibility of (SA) coordination through the oxygen atom at the hydroxyl group, absorption assigned for  $\nu(\text{OCO})_{\text{sym}}$  was noticed at the range  $1421.54\text{cm}^{-1} - 1487\text{cm}^{-1}$  while the band caused by  $\nu(\text{OCO})_{\text{asym}}$  appeared between  $1620 - 1664\text{cm}^{-1}$  also undergo hypsochromic shift which indicates the coordination of the carboxylic group to the central metal ion. The

stretching vibration band for  $\nu(\text{C}=\text{N})$  were observed in the range of  $1512 - 1606\text{cm}^{-1}$  also by undergoing hypsochromic shift which means that the nitrogen atom of 1,10-phenanthroline was involved in coordination (Triathi and Aarti (2014). Metal-nitrogen and M-Oxygen bands were further confirmed as coordination sites by the presence of the stretching vibrations of  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  around  $418\text{cm}^{-1} - 468.70\text{cm}^{-1}$  and  $511.14\text{cm}^{-1} - 545.21\text{cm}^{-1}$  respectively. Furthermore, the bands of coordinated water observed at the range of  $842\text{cm}^{-1} - 869\text{cm}^{-1}$  support the proof that there is the presence of water in the lattice of the complexes (Dilip, *et al.*, (2012), El-Ghamry *et al.*, (2013) and Shebl *et al.*, 2010).

Due to limited availability of other spectroscopic techniques such as X-ray crystallography, NMR and mass spectroscopy and on the basis of the analytical data obtained such as melting point, solubility test, conductance, elemental analysis and the spectroscopic data obtained from UV-Visible, IR, and the following octahedral geometry structures have been proposed for the new complexes.

Proposed structure



$[\text{M}(\text{SA})(\text{PHEN})(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$  (where  $\text{M} = \text{Mn}(\text{II}), \text{Cu}(\text{II}), \text{Fe}(\text{II}), \text{Zn}(\text{II}), \text{Co}(\text{II})$ )

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	<i>E. coli</i>		<i>P.a</i>		<i>S a</i>		<i>K.spp.</i>		<i>Can.spp.</i>	
	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
Salicylic Acid	0	0	0	0	0	0.3	0	0	0	0
[Mn(SA)(PHEN)(H <sub>2</sub> O)].Cl <sub>2</sub>	0	0.8	0	0.6	0	0.8	0	1.8	0	0.8
[Cu(SA)(PHEN)(H <sub>2</sub> O)].Cl <sub>2</sub>	1.1	2.5	0	0.5	1.2	1.4	1.7	2.3	0	0.9
[Fe(SA)(PHEN)(H <sub>2</sub> O)].Cl <sub>2</sub>	0	0	0	0	0	0.3	0	0.8	0	0.5

The results of the antimicrobial activity of the free ligands compared to their mixed complexes showed that the free 1,10-Phenanthroline was most active against the five organisms; *Escherichia coli*, (*E. coli*) *Pseudomonas aeruginosa* (*P.a*), *Staphylococcus aureus* (*S. a*), *Klebsiella* spp. (*K. spp.*) and *Candida* spp. (*Can. spp.*) on which the tests were carried out has compared to the free salicylic acid ligand that showed no activity against the organisms at 200 ppm and only minute activity was recorded when the concentration of the solution was increased to 500 ppm (Agwara *et al.*, 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 *et al.*, (2012).

The complexes showed identical activity 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 complexes of Fe(II) showed no activity against the test organisms at the 200 ppm, likewise at 500 ppm the activity was almost insignificant compared to the other complexes.

The complex of [Mn(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> showed no activity at 200 ppm but showed improved activity at 500 ppm on the test organisms. The order of activity of the complexes starting from the least to the most active is [Fe(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> < [Mn(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> < [Cu(SA)(PHEN)(H<sub>2</sub>O)<sub>2</sub>].Cl<sub>2</sub> (Agwara *et al.*, (2010) and Agwara *et al.*, (2013).

**Conclusion:** Mixed ligands metal complexes of 1,10-phenanthroline salicylic acid and were synthesized. The complexes were characterized using melting point, conductivity measurement, elemental analysis, UV-Visible and IR spectroscopy. The results of the physical and spectroscopic data confirmed that the ligands are chelating agents. In 1,10-phenanthroline,

coordination occurred through the two pyridinic nitrogen groups, while in the salicylic acid coordinated through the oxygen of the hydroxyl and the carboxylic groups. All the complexes synthesized were of octahedral geometry. The ligands and their respective complexes were screened against both bacterial and fungi species as a potential antimicrobial agents. The antimicrobial activities of the complexes were found to be greater than those of the free salicylic acid ligand, but the free 1,10-phenanthroline exhibited antimicrobial activity which is greater than those of the free salicylic acid ligand and the mixed ligand-metal complexes.

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