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# SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITY OF MIXED-LIGAND NICKEL(II) AND COPPER(II) COMPLEXES OF SALICYLALDEHYDE WITH 2,2′-BIPYRIDINE, 1,10-PHENANTHROLINE AND ETHYLENEDIAMINE

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## ABSTRACT

***Nickel(II) and copper(II) mixed-ligand complexes of Salicylaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine were synthesised and characterised by molar conductance, spectroscopic measurement, room temperature magnetic measurement and antimicrobial activity. The complexes showed different shades of colour and were non-electrolyte. The infrared spectra of the complexes confirmed the coordination through the lone pair of the carbonyl oxygen of the Salicylaldehyde. The electronic transitions were consistent with the adoption of five-coordinate geometry for the copper complexes and six-coordinate geometry for the nickel complexes. The microbial susceptibility testing showed that the copper complexes had stronger antifungal activity than the antibacterial activity. The antifungal activity was more pronounced at 12.5 – 100 mg/mL, while the antibacterial activity was generally restricted to 100 mg/mL. Notably, [Cu(Sal)$_2$(bipy)] showed no antifungal activity while [Cu(Sal)$_2$(en)] showed neither antifungal nor antibacterial activity. Among the nickel complexes only [Ni(Sal)$_2$(phen)] had both antifungal (except Fusarium) and antibacterial activity. [Ni(Sal)$_2$(en)] was neither antifungal nor antibacterial.***

## Introduction

Studies have shown that mixed-ligand complexes are important in analytical and other branches of chemistry (Mahdi *et al*., 2017). Salicylaldehyde and its derivatives have been used in coordination with various transition metals to form different coordination compounds. Salicylaldehyde is used in the formation of Schiff base which have been found to possess various pharmacological importance. Theoretical studies of transition metal complex of Salicylaldehyde have shown that salicylaldehyde undergoes intramolecular hydrogen bonding which exists between the aldehyde and hydroxyl group (Chung *et al*., 1998). The stability studies of copper(II) complex of salicylaldehyde and its derivatives (chloro and nitro derivatives) showed that the salicylaldehyde complex was more stable than the derivatives (Huang and Gladysz, 1988) and the antimicrobial studies have shown the activity of these complexes against some bacteria and fungi (Burton *et al*., 1964; Burton *et al*., 1965; Clarke *et al*., 1963; Rehn *et al*., 1981; Percy and Thornton, 1972). Several aldehydes derivatives studied by Pelttari *et al.,* 2007 especially the halogenated, hydroxylated and nitro salicylaldehyde, have been confirmed to have high biological activity (Pelttari *et al.,* 2007). Effect of the ligand substituent substitution on copper(II) complexes of salicylaldehyde showed the increase in M-O and C-O bond as higher electron releasing substituent was added to the salicylaldehyde ring (Percy and Thornton,1972).

Schiff base complexes prepared from aldehyde and its derivatives are of much interest because of their chemistry and potentially beneficial biological activities. The antimicrobial studies of metal(II) complexes of isatin salicylaldehyde acyldihydrazones prepared by condensing isatin, salicylaldehyde and dihydrazides exhibited excellent antifungal and antibacterial activity than the standard used (Vinod *et al*., 2012). The solvent and substituent effect on the antimicrobial activity of three different Schiff base derived from 2-aminopyridine and various substituted benzyaldehydes revealed that the activity of these compound increased in less polar solvent against S. aureus and E. coli in diverse concentrations (Gupta *et al*., 2013). There is scanty report on the synthesis and antimicrobial activities of mixed ligand copper complexes of salicylaldehyde. Therefore, the aim of this work is to synthesise, characterise and carryout the antibacterial properties of nickel(II) and copper(II) mixed ligand complexes of salicylaldehyde with nitrogen containing ligands.

## Materials and methods

### Reagents

The chemicals include; copper(II) nitrate trihydrate, copper(II) chloride hexahydrate, nickel(II) nitrate trihydrate, copper(II) bromide, 2,2′-bipyridine, 1,10-phenanthroline, Salicylaldehyde and ethylenediamine. They are of analytical grade obtained from Aldrich and BDH chemicals and were used as received.

### Synthesis of [Cu(Sal)$_2$(Phen)]

Copper(II) nitrate trihydrate (0.67 mL, 2.77 mmol) dissolved in water was added dropwisely into the mixture of Salicylaldehyde (0.30 mL, 2.77 mmol) and 1,10-phenanthroline (0.5 g, 2.77 mmol) in 10 mL methanol. The reaction mixture was stirred for 2 hours and the precipitates formed were filtered, washed with methanol and dried in vacuo.

### Synthesis of [Cu(Sal)$_2$(Bipy)]

Copper(II) nitrate trihydrate (0.67 mL, 2.77 mmol) dissolved in water was added dropwisely into the mixture of Salicylaldehyde (0.30 mL, 2.77 mmol) and 2,2′-bipyridine (0.43 g, 2.77 mmol) in 10 mL methanol. The reaction mixture was stirred for 2 hours and the precipitates formed were filtered, washed with methanol and dried in vacuo. Similar procedure was employed in the synthesis of the ethylenediamine complex.

### Synthesis of [Cu(Sal)(Phen)Cl]

Copper(II) chloride (0.47 g, 2.77 mmol) dissolved in water was added dropwisely to a mixture of Salicylaldehyde (0.3 mL, 2.77 mmol) and 1,10-phenanthroline (0.5 g, 2.77 mmol) in 10 mL methanol. KOCN (0.21 g, 2.561 mmol) dissolved in water was added to the reaction mixture and stirred for 2 hours. The precipitates formed were filtered, washed with methanol and dried in vacuo. Similar method was employed in the synthesis of the ethylenediamine and bipyridine complexes.

### Synthesis of [Cu(Sal)(Bipy)Br]

Copper(II) bromide (0.715 g, 3.201 mmol) dissolved in ethanol was added dropwisely into the mixture of Salicylaldehyde (0.30 mL, 2.77 mmol) and 2,2′-bipyridine (0.5 g, 3.201 mmol) dissolved in 10 mL methanol. KOCN (0.26g, 3.201 mmol) dissolved in water was then added to the reaction mixture and stirred for 2 hours and the precipitates formed were filtered, washed with methanol and dried in vacuo. Similar method was employed in synthesis of the ethylenediamine and bipyridine complexes.

Synthesis of [Ni(Sal)$_2$(Phen)]

Nickel(II) nitrate (0.810 g, 2.77 mmol) dissolved in water was added dropwisely to a mixture of Salicylaldehyde (0.3 mL, 2.77 mmol) and 1,10-phenanthroline (0.500 g, 2.77 mmol) in 10 mL methanol. 0.147 g $Na_2CO_3$ dissolved in water was added to the reaction mixture and stirred for 2 hours and the complex formed was filtered, washed with methanol and dried. Similar procedure was followed in the synthesis of the ethylenediamine and bipyridine complexes.

### Physical Measurements

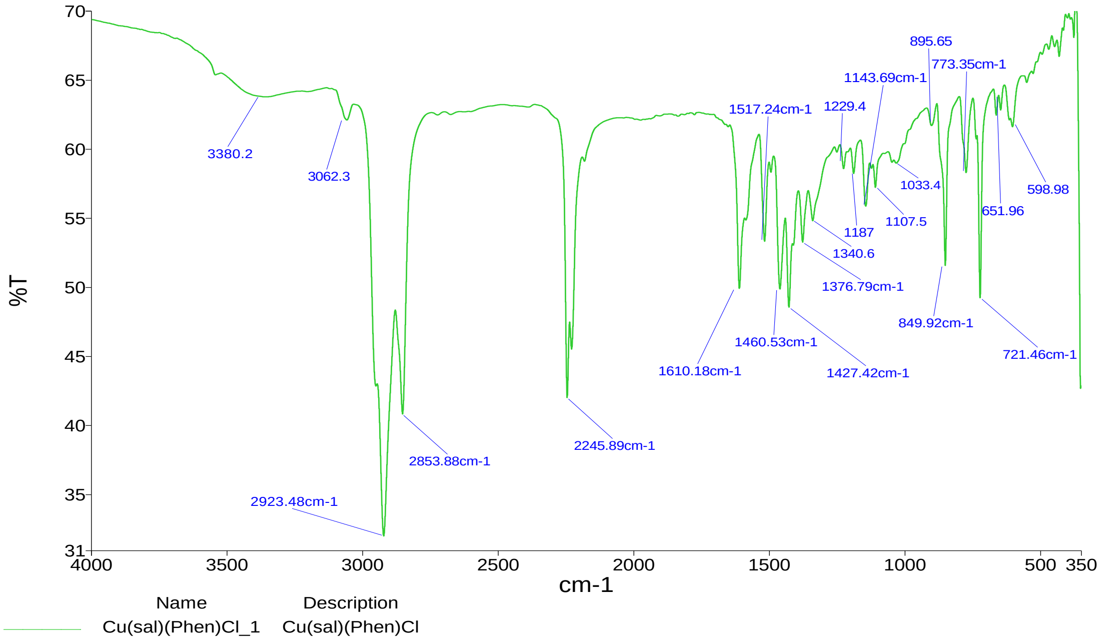
The percentage metal in the nickel(II) and copper(II) compounds were determined titrimetrically using EDTA. The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech). The antibacterial test was determined by agar-cup diffusion. The antimicrobial susceptibility testing of the complexes was carried out at the department of pharmaceutical microbiology, university of Ibadan, Ibadan, Nigeria.

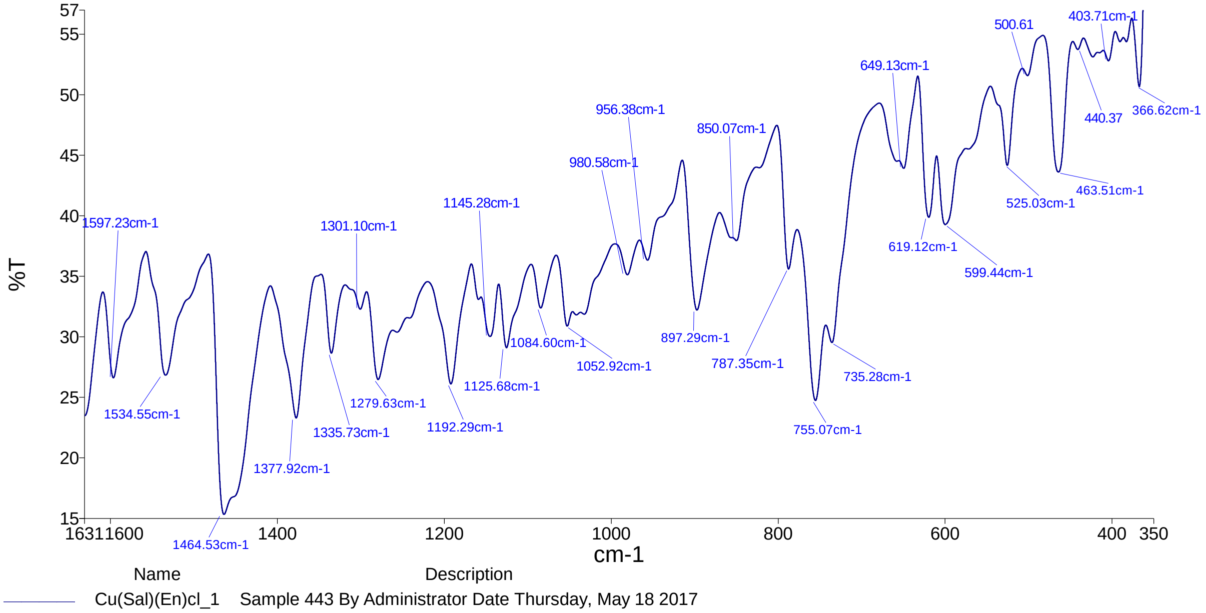
The infrared spectra were measured using nujol on Perkin Elmer Spectrophotometer 11 FT-IR. The electronic spectra of the compounds in methanol and chloroform were recorded on a Perkin Elmer Lambda double beam UV/VIS spectrophotometer using 1cm glass cell at the Department of Chemistry, University of Ibadan. The magnetic susceptibilities of the compounds at room temperature were measured using Sherwood magnetic susceptibility balance.

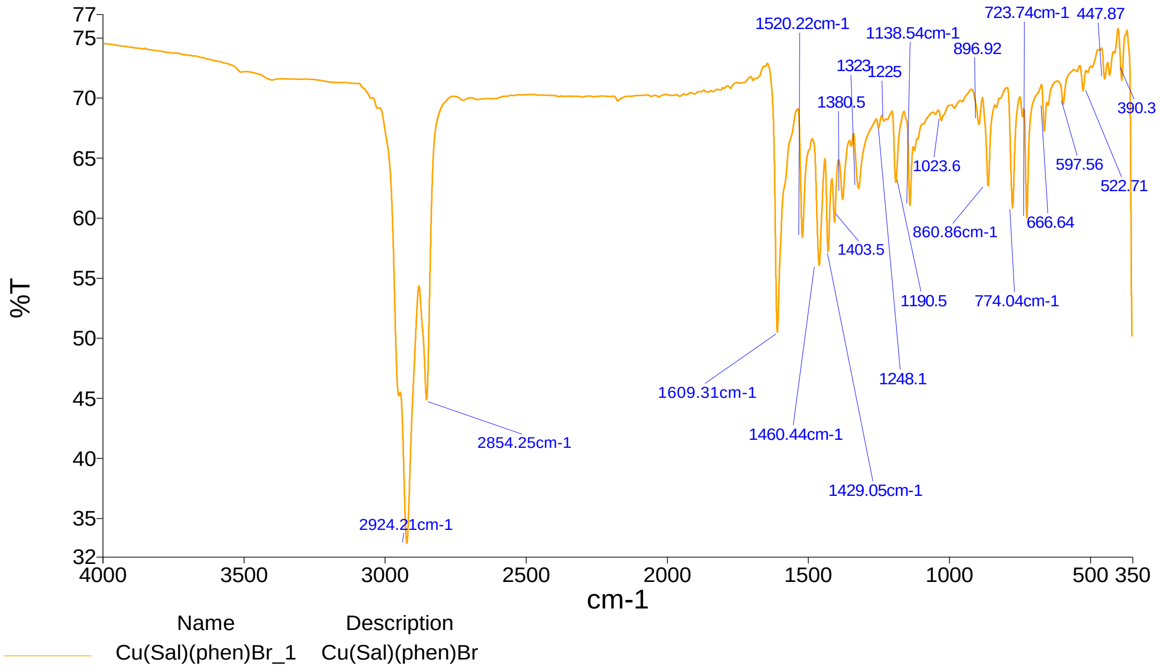
The microbiostatic activity of the synthesised compounds was determined by agar cup diffusion, using each compound in decreasing concentration of 100 mg/mL-6.25 mg/mL dissolved in methanol against every microbial isolated tested. Plate cultures were prepared either by seeding (bacteria and yeast) or spread plate (moulds) using 0.1mL of 10-2 dilution from 18 to 12 hrs. Old broth culture of each bacterium or 24 to 72 hour old broth of each fungus, in nutrient agar (bacteria) and Sabouraud dextrose agar (fungi). Each of the well dug in the set agar media was filled with three drops of the dissolved compound, 100 mg/mL followed by a pre-incubation diffusion period of 1 hr. on bench. The cultured plates were incubated at 37° C for 24 hrs. (bacteria) and 28 ° C for 24-72 hrs. (fungi). Thereafter, the antimicrobial susceptibility was assessed by observing the plates for zones of growth inhibition, measured in mm (Omoregie *et al.*, 2015).

## RESULTS AND DISCUSSION

The analytical data of the complexes, such as colours, percentage yield, melting points, and molar conductivity are presented in Table 1. All the copper(II) mixed-ligand complexes showed blue and green colours of different shades except [Cu(SAL)$_2$en] which showed black colour. Also, Nickel(II) complexes showed light green colour except [Ni(SAL)$_2$en] which showed red colour. The percentage metal analysis of the various complexes were in good agreement with those calculated for the proposed formula.







### Conductance measurement

The conductance measurement of the complexes in nitromethane showed molar conductivity in the range 33-40 ohm$^{-1}$cm$^2$ mol$^{-1}$ indicating that they were non-electrolyte. A value of 60-115 ohm$^{-1}$ cm$^2$ mol$^{-1}$ is expected for a 1:1 electrolyte (Geary, 1970).

### Magnetic moment

The magnetic moment of the compounds are shown in Table 1**.** Octahedral nickel complexes are expected to have moment in the range 2.9–3.3 B.M. while tetrahedral complexes have values in the range 3.2 – 4.1 B.M. but literature has shown that unusual moment of 2.97 and 3.78 B.M. have been reported for tetrahedral and octahedral nickel(II) complexes respectively (Patel and Woods, 1990). Our synthesised Ni complexes showed magnetic moments of 1.45, 2.22, and 3.72 B.M. The lower values observed in [Ni(SAL)$_2$Bipy] and [Ni(SAL)$_2$en] may be due to interconversion of stereochemistries and/or dimerization (Osowole *et al*., 2000). Magnetically dilute Cu(II) complexes is expected to have a magnetic moment of 1.73-2.2 B.M. (Patel and Woods, 1990b). The synthesised copper(II) complexes had moments in the range 1.70 - 2.18 B.M. which indicate their mononuclear nature and absence of dimerization.

**Table 1. Analytical and physical data of mixed ligand nickel(II) and copper(II) complexes of Salicylaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine**

| Compound | Mol. Wt. (g mol$^{-1}$) | Colour | M.pt($^o$C) | Yield % | %Metal Exp (Cal) | $\mu_{eff}$ (BM) | ($\Omega^{-1}$cm$^2$mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| [Cu(SAL)$_2$Phen] | 485.55 | Blue | 274-276 | 38 | 13.40(13.10) | 1.63 | 34 |
| [Cu(SAL)$_2$Bipy] | 461.55 | Dark green | 266-268 | 31 | 14.30(13.80) | 1.74 | 33 |
| [Cu(SAL)$_2$en] | 365.55 | Deep green | >300 | 40 | 16.15(17.38) | 1.90 | 40 |
| [[Cu(SAL)(Phen)Cl] | 400.05 | Bluish-green | 246-248 | 54 | 15.38(15.88) | 1.77 | - |
| [Cu(SAL)(Bipy)Cl] | 376.05 | Bluish green | 274-276 | 28 | 16.80(16.90) | 1.96 | - |
| [Cu(SAL)(en)Cl]5H$_2$O | 370.05 | Black | 255-257 | 67 | 17.00(17.20) | 1.55 | - |
| [Cu(SAL)(Phen)Br] | 444.45 | Dark green | 260-262 | 59 | 14.40(14.30) | 2.18 | - |
| [Cu(SAL)(Bipy)Br] | 420.45 | Dark green | 243-245 | 59 | 15.20(15.10) | 2.0 | - |
| [Cu(SAL)(en)Br | 324.45 | Dark green | 298-300 | 66 | 19.40(19.60) | 1.70 | - |
| [Ni(SAL)$_2$Phen] | 480.69 | Light green | >300 | 15 | 12.10(12.20) | 3.72 | 39 |
| [Ni(SAL)$_2$Bipy] | 456.65 | Light green | >300 | 15 | 13.20(12.90) | 2.22 | 38 |
| [Ni(SAL)$_2$en] | 360.69 | Red | >300 | 49 | 15.62(16.27) | 1.45 | 35 |

## Infrared spectra

The relevant infrared spectra of the complexes are listed in Table 2. A strong band at 1665cm$^{-1}$ in the Salicylaldehyde has been assigned as ν(C=O) which shifted to lower vibrational frequency around 1655.-1602 cm$^{-1}$ in the complexes indicating the coordination through the oxygen atom to the metal ion. The highest frequency shifts were observed in the [Cu(SAL)$_2$(Bipy)], [Cu(SAL)(Bipy)Cl] and [Cu(SAL)(Bipy)Br] complexes. The ν(C-O) band in the ligand was observed at 1278cm$^{-1}$ which also shifted to around 1280-1126cm$^{-1}$ in the metal complexes. The ν(C=N) vibrations in the 2,2'-bipyridine and 1,10-phenanthroline observed at 1581 and 1586 cm$^{-1}$ shifted upon complex formation to a lower band in the copper(II) and nickel (II) compounds confirming the coordination with the metals through the nitrogen atoms . The vibrational frequency due to the M-X halides, ν(M-N) and ν(M-O) has been observed to occur below 800 cm$^{-1}$ (Osowole and Tolulope, 2013; Chandraleka and Chandramohan, 2014).

**Table 2. Relevant infrared data of mixed-ligand nickel(II) and copper(II) complexes of Salicylaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine**

| **Compound** | **V(C=O)** | **V(C-O)** | **V(M-N)** | **V(M-O)** | **V(C=N)** | **V(M-X)** |
|---|---|---|---|---|---|---|
| SAL | 1665s | 1278s | - |  | - |  |
| Phen | - | - | - |  | 1586w |  |
| Bipy | - | - | - |  | 1581w |  |
| En | - | - | - |  | - |  |
| [Cu(SAL)$_2$Phen] | 1630s | 1227w | 509w | 433S | 1587s | - |
| [Cu(SAL)$_2$Bipy] | 1609s | 1250w | 525w | 445w | 1523s | - |
| [Cu(SAL)$_2$en] | 1648s | 1238w | 570m | 441w | - | - |
| [Cu(SAL)(Phen)Cl] | 1610s | 1226w | 599w | 430w | 1517s | 773s |
| [Cu(SAL)(Bipy)Cl] | 1602s | 1248w | 614 | 418s | 1569m | 775s |
| [Cu(SAL)(en)Cl]5H$_2$O | 1631s | 12780w | 525m | 464s | - | 787s |
| [Cu(SAL)(Phen)Br] | 1609s | 1280w | 598w | 448w | 1520s | 774s |
| [Cu(SAL)(Bipy)Br] | 1605s | 1248w | 523w | 442w | 1519w | 765s |
| [Cu(SAL(en)Br] | 1647s | 1248 | 569s | 465s | - | 751w |
| [Ni(SAL)$_2$Phen] | 1653s | 1251m | 533s | 422w | 1528s | - |
| [Ni(SAL)$_2$Bipy] | 1654s | 1252m | 533s | 437m | 1528s | - |
| [Ni(SAL)$_2$en] | 1621s | 1237m | 553w | 478s | - | - |

## Electronic spectra

The solid electronic reflectance spectra are presented in Table 3. Ligand band around 20,000 to 45,000 cm$^{-1}$ have been assigned to the π-π* and ligand to metal charge transfer transitions. In the synthesised complexes band observed around 31,250 – 31,949 have been assigned to the π-π* transition while the benzenoid/σL-3dxy transitions was observed 39,216 - 39,841 (Mahdi *et al.*, 2017; Omoregie et al., 2013; Lever, 1982; Johnson and Thornton, 1975).

**Table 3. The electronic solid reflectance spectra data of mixed ligand nickel(II) and copper(II) complexes of Salicylaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine**

| Compound | π-π* Transitions | d-d Transitions | Geometry |
|---|---|---|---|
| [Cu(SAL)$_2$Phen] | 39,841, 31,949 | 12,788 | Square pyramidal |
| [Cu(SAL)$_2$Bipy] | 39,683, 31,949 | 15,873 | Square pyramidal |
| [Cu(SAL)$_2$en] | 39,683, 31,646 | 14,923 | Square pyramidal |
| [Cu(SAL)(Phen)Cl] | 39,683, 31,949 | 15,267 | Square pyramidal |
| [Cu(SAL)(Bipy)Cl] | 39,063, 31,348 | 14,993 | Square pyramidal |
| [Cu(SAL)(en)Cl].5H$_2$O | 39,216, 31,250 | 17,212 | Square pyramidal |
| [Cu(SAL)(Phen)Br] | 39,216, 31,348 | 14,493 | Square pyramidal |
| [Cu(SAL)(Bipy)Br] | 39,063, 31,348 | 19,802 | Square pyramidal |
| [Cu(SAL)(en)Br] | 39,216, 31,447 | 17,153 | Square pyramidal |
| [Ni(SAL)$_2$Phen] | 39,063 31,348 | 16,313 | Octahedral |
| [Ni(SAL)$_2$Bipy] | 39,216, 31,250 | 16,474 | Octahedral |
| [Ni(SAL)$_2$en] | 39,216, 33,784 | 14,620 | Octahedral |

The d$^9$ configuration of copper(II) complexes are expected to have a broad band around 11,000 to 16,000 cm$^{-1}$ but can split due to tetragonal distortion which result into three transitions; $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$, and $^2B_{1g} \rightarrow {}^2A_{1g}$. Square planar copper(II) stereochemistry exhibit a broad band between 13,000 to 20,000 cm$^{-1}$, with absorption that shows little structure between 18,000 to 21,000 cm$^{-1}$ and no electronic absorption below 10,000 cm$^{-1}$ (Lever, 1982). The copper complexes showed a single broad band absorption around 14,923 to 19,802 cm$^{-1}$ which has been assigned as square pyramidal geometry. High value was observed in the [Cu(Sal)bipyBr] (19,802 cm$^{-1}$) and [Cu(Sal)enNO$_3$] (18,051 cm$^{-1}$). The electronic spectra of the Nickel complexes showed absorption bands around 14,619 to 16,474 cm$^1$ which has been assigned as the d-d bands transitions in an octahedral geometry (Lever, 1982).

## Antimicrobial study

The nickel(II) and copper(II) complexes showed varying level of antibacterial activity at 100–25.0 mg/mL concentrations with the exception of [Cu(Sal)$_2$(en)], [Cu(Sal)PhenBr], [Cu(Sal)BipyBr], [Cu(Sal)(en)Br], [Cu(Sal)(en)Cl] and [Ni(Sal)$_2$(en)] which did not inhibit *Staphylococcus auneus*, similarly against *Escherichia coli* and *Klebsiella pneunomia* by [Ni(Sal)$_2$(en)].

Notably, [Cu(Sal)$_2$(en)] failed to inhibit all the three bacterial isolate just as [Cu(Sal)BipyCl] against *Escherichia coli* (Table 4). Against the fungi tested, the copper complexes were pronounced in their inhibitory activity, particularly against *Candida albicans* with the exception of [Ni(Sal)(en)NO$_3$] that inhibited only *Pennicillin notatum* at 100 mg/mL. Other nickel complexes showed no antifugal activity. Overall, the Cu and Ni complexes could be described as been more antifungal than antibacterial in their inhibitory activity. This description agrees with our previous reports (Omoregie *et al.*, 2013). At the concentrations where the Cu and Ni complexes were found to show antimicrobial activity, they compared favourably with the standard antibiotics used; gentamycin and tioconazole against bacterial and fungi respectively.

**Table 4. Antimicrobial activity of mixed ligand nickel(II) and copper(II) complexes of Salicylaldehyde with 2,2′-bipyridine, 1,10-phenanthroline and ethylenediamine**

| Compound | SA | E.coli | Kleb | Ca | Fus | Pen |
|---|---|---|---|---|---|---|
| $[Cu(SAL)_2phen]$ | MS | MS | S | S | VS | S |
| $[Cu(SAL)_2Bipy]$ | S | MS | VS | R | R | R |
| $[Cu(SAL)_2en]$ | R | R | R | R | R | R |
| [Cu(SAL)(phen)Cl] | S | MS | S | VS | VS | VS |
| [Cu(SAL)(Bipy)Cl] | MS | R | MS | VS | VS | S |
| $[Cu(SAL)(en)Cl].5H_2O$ | R | S | S | VS | VS | S |
| [Cu(SAL)(phen)Br] | R | MS | R | VS | S | R |
| [Cu(SAL)(Bipy)Br] | R | MS | VS | VS | VS | S |
| [Cu(SAL)(en)Br] | R | R | R | VS | R | S |
| $[Ni(SAL_{)2}(phen)]$ | S | MS | VS | MS | R | VS |
| $[Ni(SAL)_2en]$ | R | R | R | R | R | R |
| Gentamycin/Tioconazole | MS | MS | MS | MS | MS | MS |
| Methanol | R | R | R | R | R | R |

VS=Very sensitive, S = Sensitive, MS = moderately sensitive, R = resistance

SA = *staphylococcus aureus*, Kleb = *klelbsiella pneumonia*, E.coli = *Escherichia coli*,

Ca = *Candida albican,* Fus = *Fusarium domesticum,* Pen = *Pennicillin notatum*

## Conclusion

The nickel(II) and copper(II) mixed ligand complexes in the form $[M(SAL)_2phen]$, $[M(SAL)_2Bipy]$ and $[M(SAL)_2en]$ coordinated to Salicylaldehyde in the ratio of 1:2 through the carbonyl oxygen, while the other six Copper(II) complexes in the form [Cu(SAL)(L)X] (where L = phen, bipy and en, X = Cl and Br respectively) showed copper-ligand coordination ratio of 1:1, and assumed five coordinate geometry. The halogen containing complexes shows more pronounce antifungal activity than the other complexes.

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