ISSN No:-2456-2165

# Synthesis, Characterization and Anti-Bacterial Activities of $Zn^{2+}$, $Cu^{2+}$ and $Fe^{2+}$ Complexes of Asparagine

*[1]Gongden, J.J, [2]Linga, P, [3]Paul, S, [4]Lawal, R.A, [5]Ranga, Y, [6]Lohdip, Y.N
[1,2,4,5,6] Department of Chemistry, University of Jos, Plateau State,Nigeria
[3]Department of chemical Sciences, Federal University of Kashere, Gombe State, Nigeria

**Abstract :- There is need for more research on complexes and their bioactivities. Complexes of copper (II), iron (II) and zinc (II) where synthesized with asparagine in the ratio of 1:2 and characterized. The melting point, colour and solubility in water, ethanol, diethyl ether, acetone, chloroform, DMSO and methanol were studied at 25ºC. The characterization of the prepared complexes was done using FT-IR, UV-VIS, XRD, and crystallography methods. The percentage yield obtained were 60.3%, 44.2% and 26.12% for Cu (II), Fe(II) and Zn (II) complexes respectively. The complexes were found to be soluble only in methanol and slightly in ethanol amongst other solvents studied at room temperature. The melting points of the complexes ranged between 230-234ºC, 292-298ºC and 285-288ºC for Cu(II), Fe(II) and Zn(II) complexes respectively while that of the ligand (asparagine) used was found to be 240-250ºC, an indication that the prepared complexes have higher melting point compared to the ligand possibly due to strong coordination. The FT-IR spectra shows that the prepared Cu(II), Fe(II) and Zn(II) complexes have tentative coordinate points at O and N atoms with confirmed UV-VIS wavelengths of 386nm, 290nm and 370nm respectively. The complexes were found to be crystalline as confirmed by the sharp peaks of their X-ray diffraction results. The crystalline size for zinc and copper complexes are 44.22 nm and 30.89 nm respectively. The crystallographic indicate that the complexes exhibit an octahedral structure for Cu(II) and Zn(II) complexes respectively. Anti-bacterial study of the synthesized complexes indicated that these complexes have anti-bacterial activity against *Staphylococcus aureus*, and *Escherichia coli*.**

***Keywords:-*** *Complexes; Synthesis; Characterization; Asparagine; Anti-bacterial.*

## I. INTRODUCTION

Inorganic complexes have long been utilized for many therapeutic purposes (Gongden et al., 2020a). They are used perhaps because of the general notion that inorganic compounds (e.g., metal complexes) are toxic, and controlled use of such a compound may suppress some biological processes. Metal complexes are promising, leading to synthetic and structural research due to their structural diversity. It is believed that the synthesis of metal complexes has a wide range of biological activities, including antibacterial, antifungal, anti-inflammatory, and antioxidant amongst others (Gongden et al., 2020b). However, the bioactivities of most coordination compounds only came to limelight in the 19th century (Gongden et al, 2020a). The synthesis of metal complexes is gaining more awareness in chemistry and biotechnology (Anastas & Warner, 1998). Metal complexation impacts significant effects on biological activities where resistance of drugs have been discovered (Gispert, 2008). In this study, asparagine, a non-essential amino acid in humans is being used as a ligand to synthesize complexes of zinc, copper and iron. The bioactivities (anti-bacteria) of the complexes are being studied for possible drug formulation of bacteria-resistant drugs.

## II. MATERIALS AND METHOD

All chemicals and reagents used were of analytical grades unless less stated. The method used for the synthesis was direct method as proposed and used by Lawal et al., 2015; Gongden et al., 2020b.

### *A. Characterization of The complexes*

Instrumental methods were used to characterize the complexes, the ligands and the metal salts. FT-IR analysis was carried out on the ligands and the complexes while UV-vis spectrophotometer was used to measure the wavelengths of the metal salts and the complexes. The FT- IR analysis of both the ligands and the complexes were recorded on FT-IR-ATR (Shimadzu 8400S model) utilizing KBr disc process and all samples were scanned over a range of 750-400$cm^{-1}$. Cu-Kα radiation was used for XRD characterization. Further characterization (conductivity measurement, colour, solubility, pH, melting point and boiling point were carried out using standard laboratory procedures) at the National Research Institute for Chemical Technology, KM 4 old Kano Road Basawa, Zaria Kaduna State and Post Graduate Laboratory, University of Jos and Multi User Laboratory A.B.U Zaria.

## III. RESULT AND DISCUSSION

The percentage yield obtained were 60.3%, 44.2% and 26.12% for Cu (II), Fe(II) and Zn (II) complexes respectively. These are in agreement with literature results for similar complexes of asparagine synthesized (Jurgen, 1996). The scanned UV-vis spectrum of Cu(II), Zn (II) and Fe(II) complexes are given in figure 1-3 and the electronic absorption spectral bands shown in Table 3. The UV-vis spectra of the complexes showed the lamda max of 290 to 386 nm as shown in Table 1. These are visible region transitions involving the electrons in the carbonyl group double bond ($\pi - \pi^*$) and the oxygen lone pair electrons respectively.

ISSN No:-2456-2165

The increase in the wave is due to complexes formation between metals and the ligand (Gongden et. Al., 2020c).

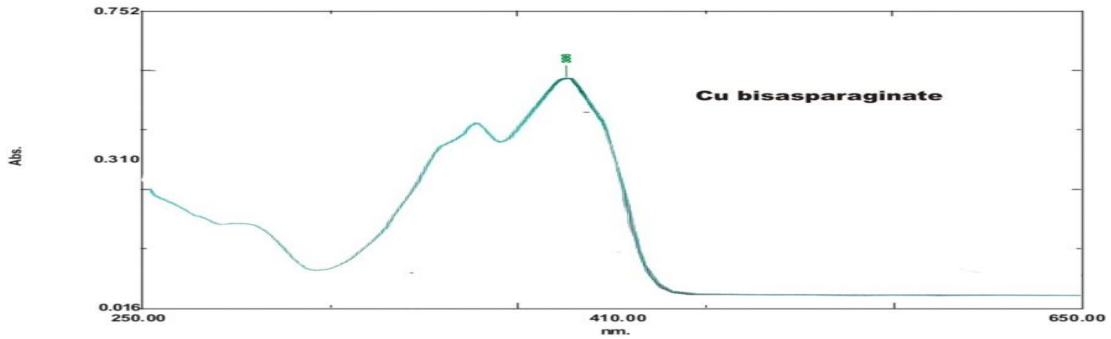


Fig. 1: UV-Vis Spectrum of Copper bisasparaginate

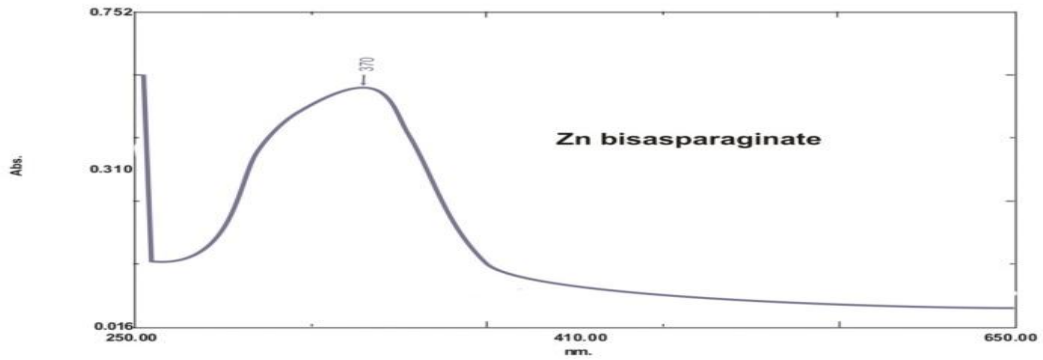


Fig. 2: UV-Vis Spectrum of Zinc bisasparaginate

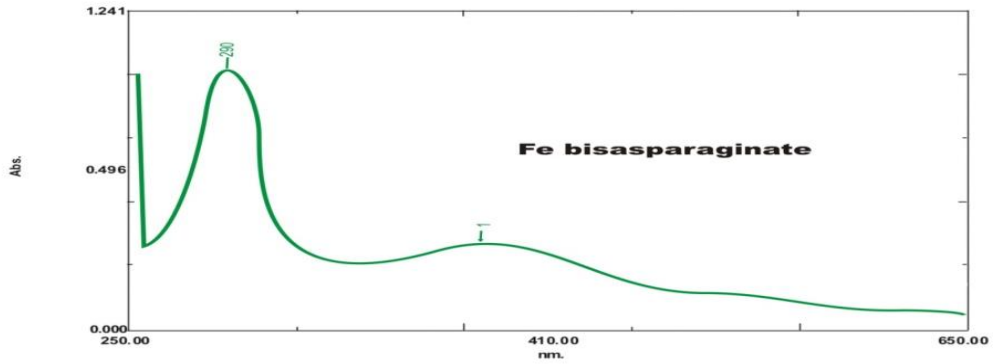


Fig. 3: UV-Vis Spectrum of Iron bisasparaginate

| Compound | Cu(II)Asn | Fe(II)Asn | Zn(II)Asn |
|---|---|---|---|
| λ max | 386 | 290 | 370 |
| absorbance | 0.610 | 0.694 | 0.694 |

Table 1: Absorption bands (λ max) of the complexes

The FT-IR spectra of the complexes provided information on the coordination mode between the ligands and the metal ion IR spectra. The IR spectra of Cu(II), Zn (II) and Fe (II) complexes and the ligand (Asn) are given in Figure 4, 5, 6, and 7, respectively. The characteristic bands of the ligand and the complexes are summarized in Table 2. The features of the IR spectra of the complexes are tabulated in the Table 1. The complexes display bands 1645-1598 and 1427-1303 $cm^{-1}$ due to v(C=O) and v(C-O) stretching respectively, significantly lower than that of free ligand v(C=O)= 1700 and v(C-O) = 1600cm-1 indicating coordination of metal ion through its carboxylate anion. The complexes showed v(N-H) bands at 3377-3377cm- which is significantly lower than the free ligand (amine base bands from 3100-3400 cm-1), clearly suggesting the coordination of amine group through Nitrogen atom of amino base.

ISSN No:-2456-2165

| Compound | OH $cm^{-1}$ | N - H $cm^{-1}$ | C - O $cm^{-1}$ | N –C $cm^{-1}$ | C =O $cm^{-1}$ |
|---|---|---|---|---|---|
| Asn | 3436.6 | 2922.2 | 1288.7 | 2267.8 | 1725.2 |
| Cu(Asn) | 1427.6 | 3380.7 | 1287.5 | 2278.9 | 1681.0 |
| Fe(Asn) | 1401.5 | 3377.0 | 1312.2 | 2240.1 | 1684.8 |
| Zn(Asn) | 1360.5 | 3377.7 | 1233.7 | 2242.5 | 1625.1 |

Table 2: Characteristic bands of the ligand and the corresponding complexes

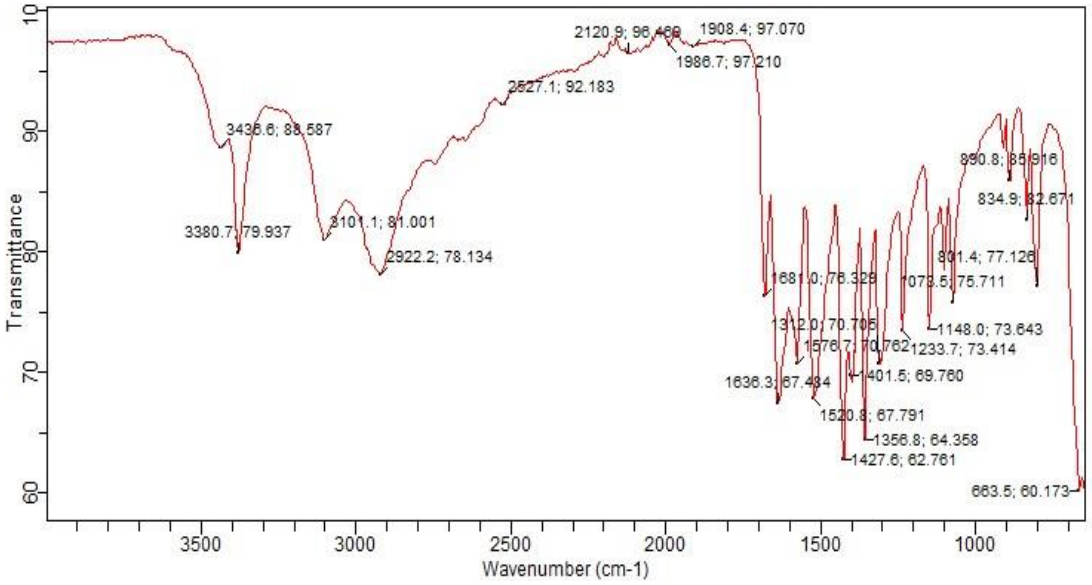


Fig. 4: FT-IR Spectrum of Asparagine

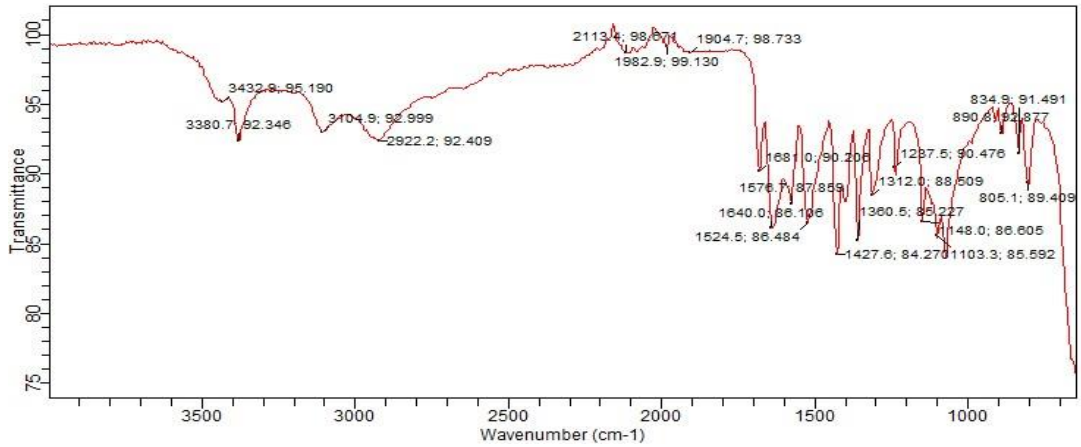


Fig. 5: FT-IR Spectrum of Copper bisaparaginate

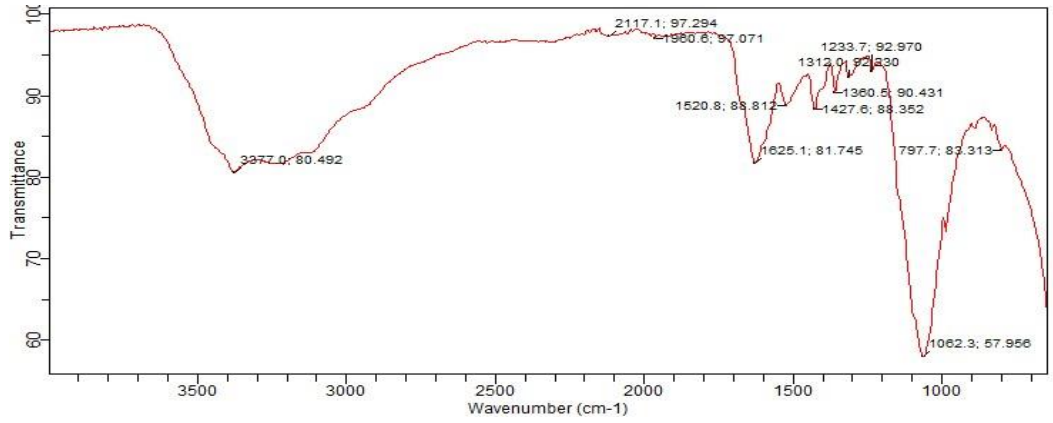


Fig. 6: FT-IR Spectrum of Zinc Bisaparaginate

ISSN No:-2456-2165

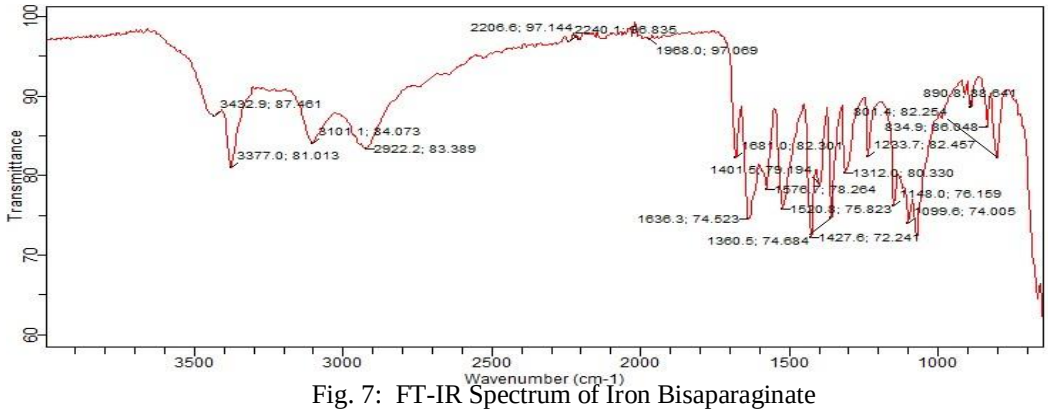


Fig. 7: FT-IR Spectrum of Iron Bisaparaginate

The X-ray diffraction patterns of the complexes are indicative of their crystalline nature. The diffraction pattern of the complexes recorded at $2\theta$ ranging from 10° to 75°. The crystalline size of the samples is estimated using the Scherrer's formula $D=k\lambda/\beta_{2\theta}\cos\theta$ here k is a constant taken to be 0.94, $\lambda$ the wavelength of X-ray used ($\lambda$=0.154 nm) and $\beta_{2\theta}$ full width at half maxima of all peaks of the XRD patterns, $\theta$ is Bragg angle. The diffraction patterns have been successfully indexed (Khan et. al,1998). The crystalline size was found for zinc and copper complex to be 44.22 nm and 30.89 nm respectively. That of iron was difficult to obtain due to its amorphous nature. It is observed that crystalline size is different for Cu(II) and Zn(II) complexes this is due to change in the R position. From the XRD pattern, zinc is more crystalline which shows very sharp peaks follow by copper complex. Iron complex is not sharp but short, possessing a kind of amorphous nature. The combine XRD patterns are shown in Figure 8 while Figures 9 and 10 show the crystal structures of zinc and iron complexes respectively. The crystal structure representations of zinc and iron bisasparaginate complexes revealed that of a distorted octahedral.

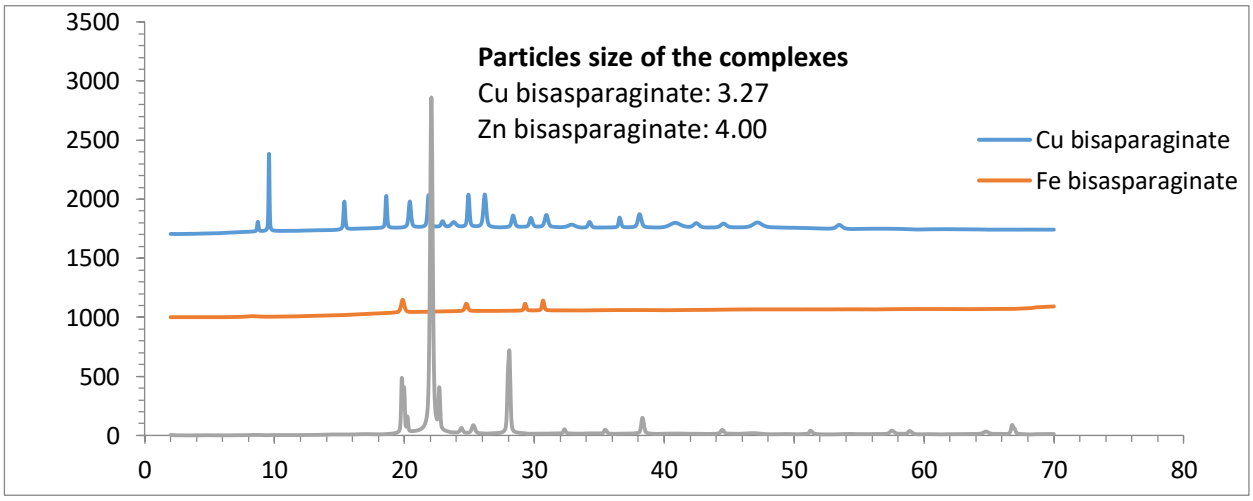


Fig. 8: The XRD Spectrum of the complexes

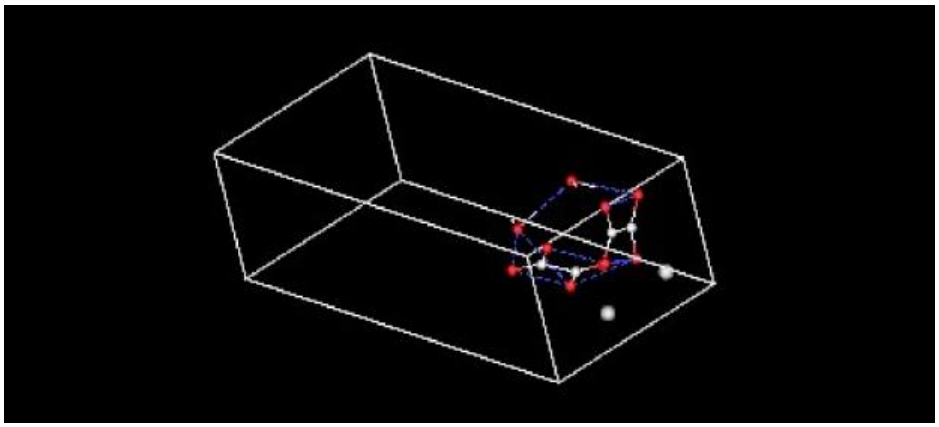

Fig. 9: Crystallographic Structure of Copper Bisasparaginate

ISSN No:-2456-2165

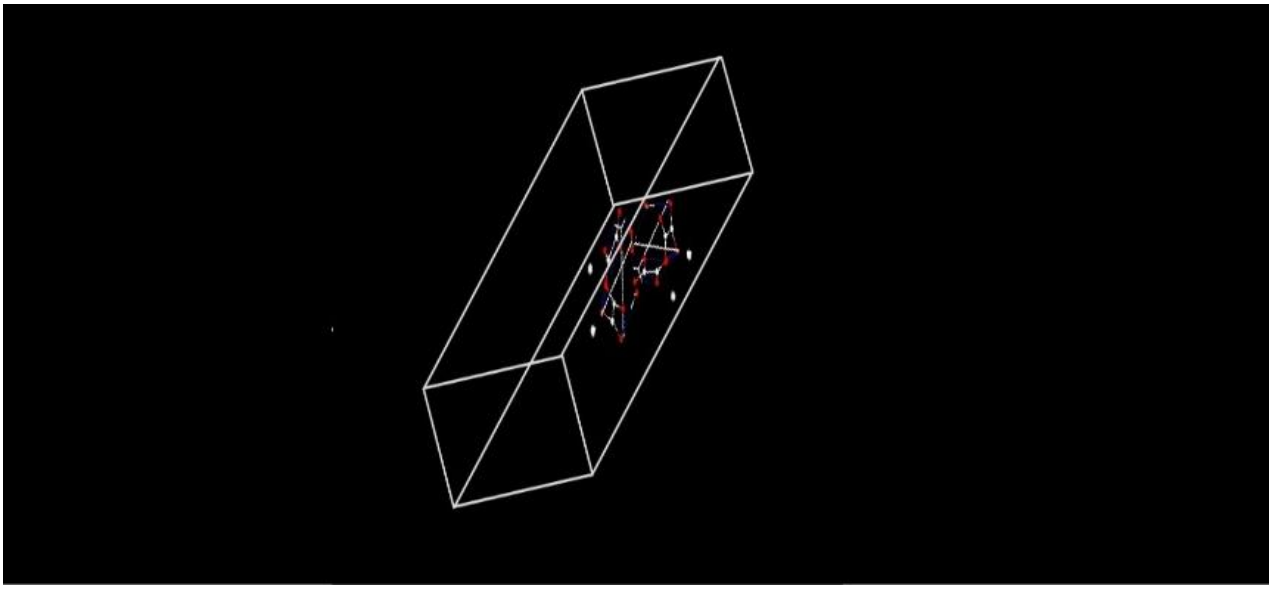

Fig. 10: Crystallographic Structure of Zinc Bisasparaginate

Table 3 shows zone of inhibition of all the metal complexes against *E. coli*, *Staphylococcus aereus*. At lower concentration, no inhibition zone was found, whereas at concentrations like 100 mg and 200 mg, all the synthesized metal complexes shown low inhibitory zones varying in the ranges 24.00 – 28.00 mm/mg zone of inhibition. Literature reveals that metal ions, geometry of metal ions and the counter ions impact great effects on the inhibition of bacterial activities. The results for *E. coli* show that iron asparaginate complex is found to be moderate. The reason may be attributed to geometries and presence of counter ions. In case of the activities of all the synthesized metal complexes against *Staphylococcus aereus,* it has been observed that all the metal complexes show intermediate inhibition zone at higher concentration. Similar to studies by Chohan et. al., (2002).

Table 4 shows that at higher concentrations all the complexes showed intermediate inhibitory zones for *E.coli* and *Staphylococcus aereus.* Overall, it may be revealed from the data given in Tables 3 – 4 that complexes of copper bisasparaginate, zinc bisasparaginate, and iron bisasparaginate are moderately active against the tested bacterial strains. The results for antibacterial activities show that the complexes inhibit bacterial growth significantly different from each other (Lohdip & Aguiyi, 2013).

| **Complexes** | **Microorganism** | **Concentration (mg/ml)** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **200** | **100** | **50** | **25** | **12.5** | **C (10)** |
| Zinc | *Staphylococcus aereus* | 28.00 | 24.00 | 20.00 | 0.00 | 0.00 | 24.00 |
| | *Escherichia coli* | 25.00 | 20.00 | 15.00 | 0.00 | 0.00 | 24.00 |
| Iron | *Staphylococcus aereus* | 24.00 | 20.00 | 0.00 | 0.00 | 0.00 | 24.00 |
| | *Escherichia coli* | 20.00 | 14.00 | 20.00 | 0.00 | 0.00 | 24.00 |
| Copper | *Staphylococcus aereus* | 24.00 | 10.00 | 20.00 | 0.00 | 0.00 | 24.00 |
| | *Escherichia coli* | 30.00 | 24.00 | 20.00 | 0.00 | 0.00 | 24.00 |

Table 3: Zone of Inhibition Concentration (mm/mg)

Key: Zone of inhibition = mm
Concentration = mg/ml
Positive control = Gentamycin 10mg/ml

| **Complexes** | **Microorganism** | **Concentration (mg/ml)** | | | | | **MIC** |
|---|---|---|---|---|---|---|---|
| | | **200** | **100** | **50** | **25** | **12.5** | |
| Zinc | *Staphylococcus aereus* | - | - | - | + | + | 50 |
| | *Escherichia coli* | - | - | + | + | + | 100 |
| Iron | *Staphylococcus aereus* | - | - | + | + | + | 100 |
| | *Escherichia coli* | - | - | + | + | + | 100 |
| Copper | *Staphylococcus aereus* | - | + | + | + | + | 200 |
| | *Escherichia coli* | - | - | + | + | + | 100 |

Table 4: Minimum Inhibitory Concentration MIC

ISSN No:-2456-2165

## IV. CONCLUSION

The synthesis and characterization of complexes of Cu(II), Zn(II) and Fe(II) was successful. The melting points of the complexes ranged between 230-234$^{O}$C, 292-298$^{o}$C and 285-288$^{o}$C for Cu(II), Fe(II) and Zn(II) complexes respectively. The FT-IR spectra data show that the prepared Cu(II), Fe(II) and Zn(II) complexes have tentative coordinate points at O and N atoms with confirmed UV-VIS wavelengths of 386nm, 290nm and 370nm respectively. The complexes were found to be crystalline as confirmed by the sharp peaks of their X-ray diffraction results. The crystalline size for zinc and copper complexes are 44.22 nm and 30.89 nm respectively. The electronic spectral data are in conformity with the transitions of octahedral complexes. Base on the above analysis the structure of the complexes of Cu(II) and Zn(II) have been proposed to be distorted octahedral. The crystalline size was found for zinc and copper complex to be 44.22 nm and 30.89 nm respectively. The antibacterial activities of all the complexes on *staphylococcus* and *E.coli* are said to be moderate at 200mg/ml.

## REFERENCES


[1.] Anastas, P.T. and Warner, J.C. (1998) Green Chemistry: Theory and Practice. Oxford University Press, Oxford.

[2.] Chohan, Z.H. et al., (2002). Antibacterial copper(II) complexes of 1,1′-symmetric ferrocene-derived Schiff-base ligands: studies of the effect of anions on their antibacterial properties, *Appl. Organomett. Chem*. 16, 17-20.

[3.] Gispert, J.R. (2008). Coordination chemistry. Weinheim: Wiley- VCH. 103-107.

[4.] [a]Gongden, J.J., Gurumyen, K.K., Kagoro, M.L., Uduah, O.V., Goji, S. Y. and Lohdip,Y.N. (2020). Synthesis and spectroscopic characterization of iron (iii) plant-based 1458xalate complex from S*pinacia Oleracea* (spinach). *Nigerian Research Journal of Chemical Sciences. V*ol. 8, Issue 1,

[5.] [b]Gongden J.J, Uduah O.V, Gurumyen K.K & Lohdip Y.N (2019). Isolation and spectroscopic characterization of urea from human urine. *International Journal of Applied and Natural Sciences (IJANS)*. Vol. 8, Issue 4. Pp. 171–180.

[6.] [c]Gongden, J. J., Gurumyen, K. K, Danja, B. A., Uduah, O. V. and Lohdip Y. N. (2020). Synthesis and pH-metric determination of the stability constant of iron (III) plant-based 1458xalate complex. *Nigerian Journal of Chemical Research.* Vol. 25 No. 1 (2020). https://www.ajol.info/index.php/njcr/issue/view/19014

[7.] Jurgen, (1996). Xenon diffusion in zeolite NaY: Transition- state theory with dynamical corrections. The Journal of physical chemistry, 100(1), 4582-4590.

[8.] Lawal. A., Amolegbe, S.A., Rajee, A.O., Babamale, H.F., Yunus M.T. (2015). Synthesis, characterization and antimicrobial acyivity of mixed as corbic and nicotinamide metal complexes. Bayero Journal of pure and applied sciences 8(1) 139-142

[9.] Lohdip, A.M. and Aguiyi, J.C. (2013). Some pharmacological activities of hexadec-12- enoic acid isolated from chenopodium ambrosioides linn. Global Journal of pure and applied chemistry research 1(2), 12-21.