Co(II), Ni(II), Cu(II) and Zn(II) Complexes: A Convenient Synthetic Routes, Spectroscopic Characterization and Antimicrobial Activity

Ibrahim Ado[1], Junaidu Na'aliya[1], Mustapha Muhammad Haleelu[2] and Salihu Sani [3]

[1]Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B 3011, Kano, Nigeria.
[2]Department of Chemistry, Federal university Dutsanma Katsina, Nigeria
[3]Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria

DOI: 10.29322/IJSRP.12.06.2022.p12644
http://dx.doi.org/10.29322/IJSRP.12.06.2022.p12644

Paper Received Date: 2nd June 2022
Paper Acceptance Date: 16th June 2022
Paper Publication Date: 20th June 2022

Abstract- The Schiff base ligand, which was prepared and used to synthesize Co(II), Ni(II), Cu(II), and Zn(II) complexes, was obtained by condensation reaction of 2-hydroxy-1-naphthaldehyde with 4-aminobenzoic acid (H_2L). The Schiff base ligand and their metal complexes were characterized by FT-IR, PXRD, magnetic susceptibility, conductance measurements, and CHN analyses. A band at 1626 cm^{-1} in the FT-IR spectra of the ligand has been linked to v(C=N) stretching vibrations. This band was shifted in the complexes' spectra (1610 – 1633 cm^{-1}), demonstrating that the azomethine group is involved in complexation. Complexes have a molar conductance of 9.54 – 14.84 $Ohm^{-1}cm^2mol^{-1}$, indicating the non-electrolytic nature. Magnetic susceptibility measurements of Co(II), Ni(II), and Cu(II) complexes showed magnetic moments between 2.80 and 5.40 BM. Square-planar geometry corresponds to the values. A diamagnetic behavior is shown by the magnetic moment value of the Zn(II) complex. The observed and computed percentages of the elements agree well according to the CHN elemental analysis of the complexes. Disc diffusion was used to evaluate the synthesized compounds for antibacterial activity against two-gram negative bacteria, *Escherichia coli* and *Salmonella typhi*, as well as certain fungal pathogens (*Candida albican*, *Aspergillus fumigatus*, and *Aspergillus flavus*). In comparison to Schiff base ligands, metal(II) complexes demonstrated more biological activity.

Index Terms- Antimicrobial activity, Complexes, Schiff base, 4-aminobenzoic acid, 2-hydroxy-1-naphthaldehyde.

I. INTRODUCTION

Mechanochemical reaction is a chemical reaction generated by the input of mechanical energy, usually by grinding or shaking to induce reactions, and it is a growing area of research for chemists [1], [2]. It's widely utilized due of its operational simplicity, increased reaction rate, high selectivity, and lower environmental impact than other procedures because it eliminates the need of aromatic solvents [3]. Another advantage of this method is that it reaches great efficiency in a shorter time. In addition, mechanochemical synthesis requires fairly basic equipment that is commonly found in chemistry laboratories [4].

A Schiff base is formed when amines are added to a compound with a carbonyl functional group. An aldehyde or ketone can be used as the carbonyl functional group. A Schiff base functions as a ligand because it often comprises -N and –O donor atoms [5]–[7]. Schiff bases with aryl substituents are far more stable and easier to prepare, whereas those with alkyl substituents are much more unstable and polymerizable. The nature of the substituents near to the imino nitrogen affects the Schiff base's complexing action. Schiff base complexes containing transition, inner transition, and non-transition metal ions have been synthesized and characterized.

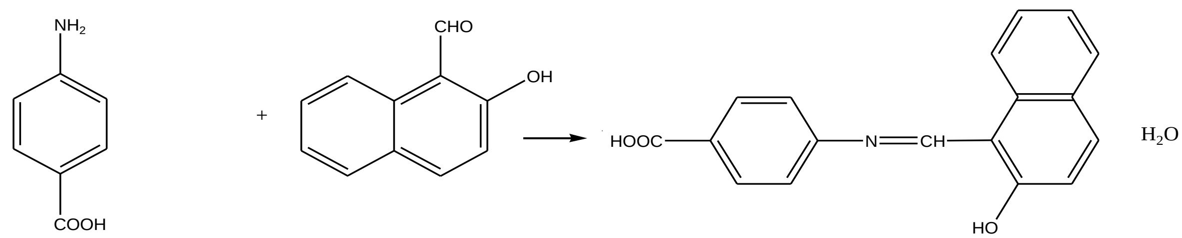
Antibiotics have been produced to treat a wide range of bacterial infections. Bacteria are becoming antibiotic resistant as a result of widespread usage or misuse of antibiotics, posing an increasing hazard to human health. As a result, mortality rates rise [8]. Researchers are designing and synthesizing novel antibacterial compounds in response to the demand for effective therapeutics against multidrug-resistant bacteria [9], [10]. Transition metal Schiff base complexes comprising ligands with nitrogen and oxygen donors have been shown to have antibacterial action. The mechanochemical synthesis and characterization of some metal(II) Schiff base complexes are described in this work.

II. MATERIALS AND METHODS

All chemical compounds and reagents were purchased from Sigma-Aldrich as analytical grade and used without additional purification. The C, H, and N content of the synthesized complexes were determined using a Euro Vector EA3000 elemental analyzer at the Birla Institute of Technology's central instrumentation facilities in India. Powder x-ray diffraction was performed at Birla Institute of Technology's core instrumentation facilities using X'Pert Pro X-ray diffractometer. A Perkin-Elmer 1000 FT-IR spectrometer was used to evaluate FT-IR spectra in the 4000-400 cm^{-1} region at Bayero University Kano's Department of Biochemistry. Elico melting point device was used to determine melting point. The molar conductance measurements of the complexes in DMF at room temperature was determined using the conductivity Meter Lab CDM-210. Gouy balance-PICO was used to determine magnetic susceptibility.

A. Synthesis of Schiff base (H_2L)

During the synthesis, 2-hydroxy-1-naphthaldehyde (0.1722 g, 1 mmol) and 4-aminobenzoic acid (0.1371 g, 1 mmol) were weighed carefully into a mortar. The reactant mixture was crushed (grinded) for 45 minutes to get a pale brown colored product. The powdered product was taken out of the mortar and allowed to air dry [10].



Scheme 1: Synthesis of Schiff base (H_2L)

B. Synthesis of [M(L)₂] complex

The metal complexes were synthesized by grinding the reaction mixture of the metal(II) acetate (1mmol) and Schiff base (0.2923 g, 1 mmol) 1:1 mole ratio in a mortar with pestle for 1hour and obtained coloured powder complexes. (M = Co, Ni, Cu or Zn) [10].

C. Antibacterial activity test

The isolate's inoculum, which comprised *S. aureus*, *E. coli*, and *S. typhi*, was swabbed onto the surface area of the prepared and solidified nutrient agar plates. The prepared solution of the test compounds and the reference antibiotic concentration made (ciprofloxacin) were put in the inoculation plates' agar wells. After a 24-hour incubation period at 37°C, the inhibitory zones was assessed [11].

D. Antifungal activity test

The isolate's standard inoculum, which included *C. albican*, *A. flavus*, and *A. fumigatus*, was swabbed onto the surface of the prepared and solidified potato agar in separate petri-dishes. At intervals of 15 mm, the solution of the compounds and the standard antibiotic (Ketoconazole) were placed inside the wells of the inoculated media. After 72 hours of incubation at 37°C, the inhibitory zone was evaluated [11].

III. RESULTS AND DISCUSSION

Schiff base ligand and its metal complexes were synthesized using mechanochemical process with a percentage yield of 77.4 – 89.5%. The compounds synthesized were coloured. Schiff base ligand was discovered to be crystalline solids with a melting point of 198 °C. Complexes have a greater decomposition temperature (277 – 298 ºC) than Schiff base melting point, indicating that they are more stable thermally (Table 1).

The result of molar conductance measurement of complexes using DMF solvent (10^{-3} M) are in the range of 9.54 – 14.87 $Ohm^{-1}cm^2mol^{-1}$ (Table 1) and the values been found to be very low to account for any dissociation of the complexes in DMF indicating its non-electrolytic nature [12].

The magnetic susceptibility of the complexes was measured at room temperature and the magnetic moments were shown in Table 1. The effective magnetic moment of [Co(L)], [Ni(L)] and [Cu(L)] are 2.80 – 5.40 BM seems to be higher than the normal values reported for tetrahedral geometries (1.7–1.8), this could be due to the presence of interactions between ethanol solvent molecules and the metal complexes or due to the presence of ferromagnetic interactions [13]–[15]. The values reported where similar with the values reported by [16] which suggest tetrahedral geometries around the metal ion. The magnetic moment value of Zn(II) complex indicate a diamagnetic behaviour consistent with the 0 unpaired electron of d^{10} species. Therefore, the Schiff bases coordinates to Zn(II) ion as four-dentate chelating agent with a tetrahedral geometry.

The Schiff base and metal complexes are soluble in DMF, DMSO and slightly soluble in acetonitrile, chloroform, diethyl ether and insoluble in n-hexane indicating that the compounds are polar (Table 2).

The azomethine stretching vibration is responsible for the strong band seen in the spectra of H_2L ligand at 1626 cm^{-1} [17], [18]. When compared to the complexes the azomethine stretching frequency moved to new frequencies (1510 – 1633 cm^{-1}) as a result of coordination of metal center with azomethine nitrogen group (Table 3). The new bands appeared at 419 - 456 cm^{-1} for

M-O vibrations and 508 - 571 cm^{-1} for M-N vibrations, which were not present in the spectra of the Schiff base [19], [20]. The presence of M-O and M-N vibrations imply that O and N atoms are involved in metal ion complexation [21]–[23].

Furthermore, the IR spectra of complexes present evidence for the coordination between the transition metal ions and acetate molecules due to the characteristic stretching *v*(C=O) mode of carbonyl occur in the range of 1704 – 1659 cm^{-1}. It can be suggested that the metal(II) coordination occur through the oxygen atom of acetate molecule and O-H of water molecule [24] in addition to azomethine nitrogen and phenolic oxygen. The increase in bond order of C=O connected with the increase in bond order C-O may give rise to coupling vibration of the bonds appeared in the range of 1556 – 143 cm^{-1} and 1473 - 1465 cm^{-1} which may be considered as associated with the respective antisymmetric and symmetric stretching modes of C-O group at the chelating site [25].

The infrared spectra of complexes also show the expected absorptions due to the stretching (3059 - 3405 cm^{-1}) bending (1659 – 1622 cm^{-1}) and wagging (501 – 545 cm^{-1}) modes of water molecules [20] which indicate the presence of coordinated water molecules as [26] reported similar values (3418, 1631 and 546 for stretching bending and wagging modes respectively).

Table 1: Properties, molar conductance and magnetic susceptibility of Schiff base complexes

Molecular Formula	Colour	Melting point (ºC)	Decomposition Temp. (ºC)	Yield (%)	Molar conductance ($Ohm^{-1}cm^2mol^{-1}$)	μ_{eff}(BM)
H_2L ($C_{18}H_{13}NO_3$)	Pale brown	198	-	87.5	-	-
[Co($C_{20}H_{17}NO_6$)]	Light Pink	-	270	89.2	9.54	2.95
[Ni($C_{20}H_{17}NO_6$)]	Yellow	-	298	90.3	12.69	2.80
[Cu($C_{20}H_{17}NO_6$)]	Peach	-	294	89.5	14.87	5.40
[Zn($C_{20}H_{17}NO_6$)]	Maroon	-	277	77.4	9.90	--

Key: (H_2L) = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 4-aminobenzoic acid.

Table 2: Solubility Test of Schiff base (H_2L) and its metal complexes

Molecular Formula	DMF	DMSO	Acetonitrile	Diethyl ether	Chloroform	Acetone	N-hexane
H_2L ($C_{18}H_{13}NO_3$)	S	S	SS	SS	SS	SS	IS
[Co($C_{20}H_{17}NO_6$)]	S	S	SS	SS	SS	SS	IS
[Ni($C_{20}H_{17}NO_6$)]	S	S	SS	SS	SS	SS	IS
[Cu($C_{20}H_{17}NO_6$)]	S	S	SS	SS	SS	SS	IS
[Zn($C_{20}H_{17}NO_6$)]	S	S	SS	IS	IS	IS	IS

S-Soluble, SS- Slightly soluble, IS- Insoluble

Table 3: Infrared spectra result of Schiff base (H_2L) and its complexes

Molecular Formula	v(OH) cm^{-1}	v(C=N) cm^{-1}	v(M-O) cm^{-1}	v(M-N) cm^{-1}
H_2L ($C_{18}H_{13}NO_3$)	3335	1626	-	-
[Co($C_{20}H_{17}NO_6$)]	3405	1633	419	571
[Ni($C_{20}H_{17}NO_6$)]	3070	1610	456	549
[Cu($C_{20}H_{17}NO_6$)]	3052	1622	452	553
[Zn($C_{20}H_{17}NO_6$)]	3059	1610	430	508

Table 4: Elemental Analysis of Schiff base complexes.

Molecular Formula	C (%) Found(Calculated)	H (%) Found(Calculated)	N (%) Found(Calculated)
[Co($C_{20}H_{17}NO_6$)]	55.51(56.35)	4.84(4.02)	3.94(3.29)
[Ni($C_{20}H_{17}NO_6$)]	55.98 (56.38)	4.39 (4.02)	3.53 (3.29)
[Cu($C_{20}H_{17}NO_6$)]	55.50(55.75)	4.20(3.98)	3.53(3.25)
[Zn($C_{20}H_{17}NO_6$)]	55.69(55.51)	4.24 (3.96)	3.62 (3.24)

Powder x-ray diffraction patterns of the mechanochemical products indicate the crystalline nature of the synthesized compound. The powder x-ray diffraction patterns of Schiff base was different from that of the reactants (2-hydroxy-1-napthaldehyde and 4-aminobenzoic acid). New peaks corresponding to the mechanochemical product were observed indicating the formation of new phase (Fig. 1).

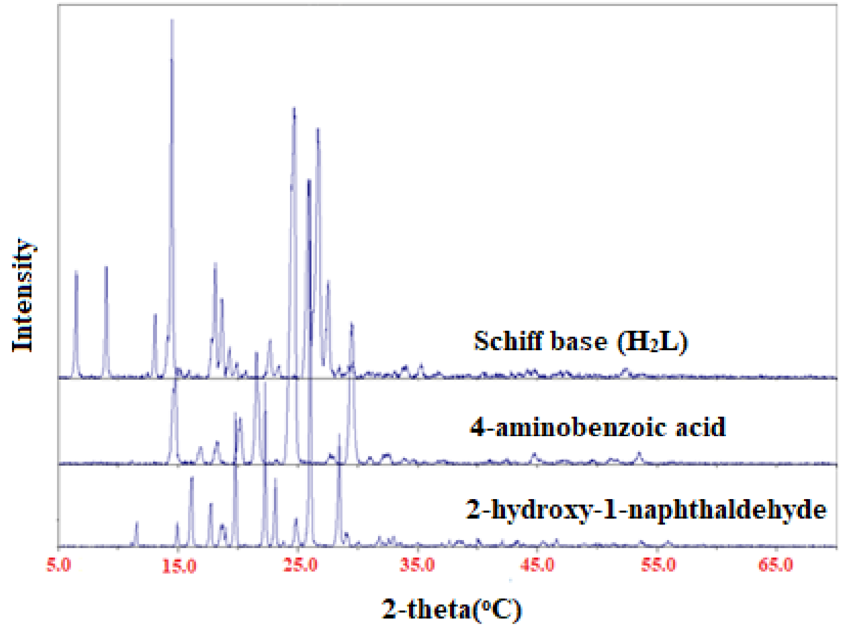


Fig. 1: Powder x-ray diffraction patterns of H_2L Schiff base, 4-aminobenzoic acid and 2-hydroxy-1-napthaldehyde showing different reflection peaks

The elemental analysis of the synthesized complexes (Table 4) shows 1:1 (metal to ligand ratio) stoichiometry. Both experimental and theoretical results of carbon, hydrogen and nitrogen have a high degree of agreement to each other which support the proposed structures of the synthesized complexes. Slight differences in some of the values are within the acceptable limit explained by [27].

The antibacterial sensitivity test results revealed that metal(II) complexes shows more toxic to the tested bacterial strains than the Schiff base Ligand. The highest antibacterial activity of the complexes was observed at 60 $mgml^{-1}$ concentrations against *E. coli* (Fig. 2). Schiff base shows moderate antibacterial activity against *S. aureus* especially at higher concentration. On the other hand, the Schiff base showed weak antifungal activity towards *C. albican*. For the complexes, the highest activity was observed against *C. albican* and *A. fumigatus* with inhibition of 16 mm each at 60 $mgml^{-1}$ concentration (Fig. 3). The antibacterial properties of Schiff base compounds have been linked to the Azomethine group [28]–[30].

The complex's antibacterial activity was improved by overlapping the ligand orbital with the metal orbital, which results in a partial sharing of the positive charge of metals with the donor group on the ligand. This coordination reduces the polarity of the metal, making it more lipophilic to the lipid layer of the bacterial cell membrane [31].

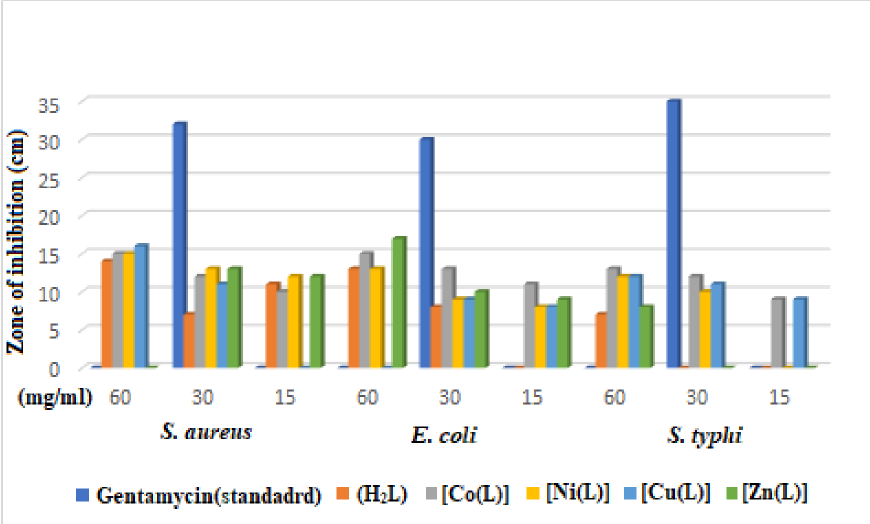


Fig. 2: Antibacterial activity result

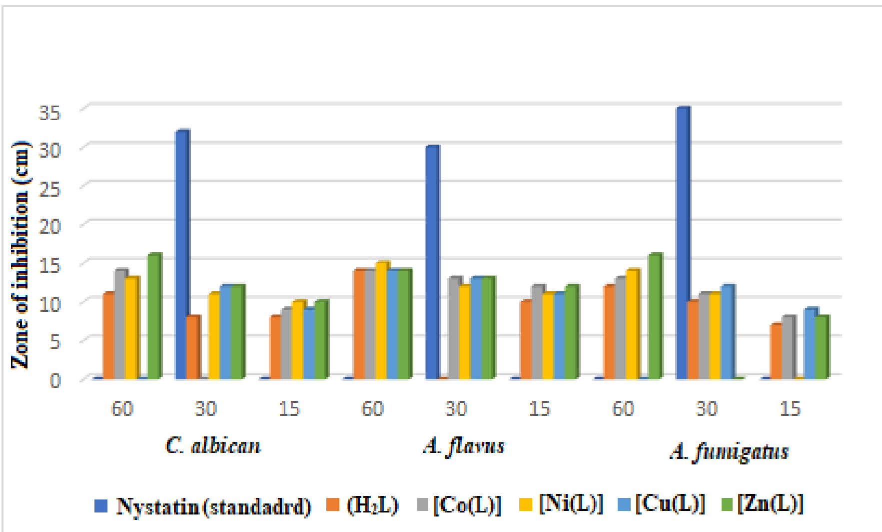


Fig. 3: Antifungal activity result

The proposed tentative structure of complexes is given in Figure 1 based on the results obtained.

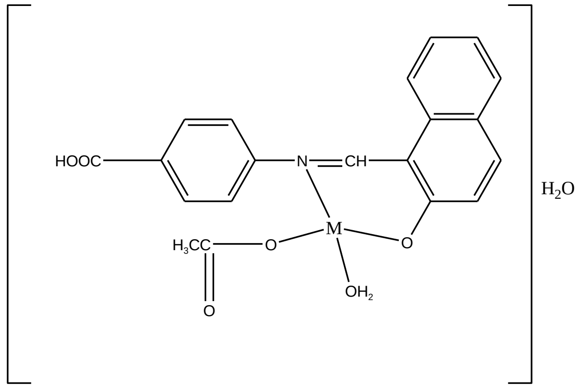


Fig. 1. Proposed structure of Complexes. Where M = Co^{2+} Ni^{2+} Cu^{2+} or Zn^{2+}

IV. CONCLUSION

Mechanochemical reaction was used to synthesize Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes derived from 2-hydroxy-1-naphthaldehyde with 4-aminobenzoic acid. FTIR, PXRD, melting point/decomposition temperature, conductivity measurement, magnetic susceptibility, and CHN analysis were used to evaluate the complexes' compositions and structures. The metal complexes were four-coordinated by the Schiff base ligand's two phenolic oxygen and two azomethine nitrogen atoms. Antimicrobial activity study on Schiff base and complexes suggest that metal complexes have higher activity than Schiff base. Mechanochemical synthesis is faster and less chemical contaminants than solvent synthesis.

REFRENCES

[1] D. Braga, L. Maini, and F. Grepioni, "Mechanochemical preparation of co-crystals," *Chemical Society Reviews*, vol. 42, no. 18, pp. 7638–7648, 2013.

[2] P. Panneerselvam, R. R. Nair, G. Vijayalakshmi, E. H. Subramanian, and S. K. Sridhar, "Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents," *European journal of medicinal chemistry*, vol. 40, no. 2, pp. 225–229, 2005.

[3] M. Gopalakrishnan, P. Sureshkumar, V. Kanagarajan, and J. Thanusu, "New environmentally-friendly solvent-free synthesis of imines using calcium oxide under microwave irradiation," *Research on Chemical Intermediates*, vol. 33, no. 6, pp. 541–548, 2007.

[4] T. Friscic and W. Jones, "Recent advances in understanding the mechanism of cocrystal formation via grinding," *Crystal Growth and Design*, vol. 9, no. 3, pp. 1621–1637, 2009.

[5] H. N. Aliyu and U. Sani, "Synthesis, characterization and biological activity of manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) schiff base complexes against multidrug resistant bacterial and fungal pathogens," *International Research Journal of Pharmacy and Pharmacology*, vol. 2, no. 2, pp. 40–44, 2012.

[6] A. A. Emara, "Structural, spectral and biological studies of binuclear tetradentate metal complexes of N3O Schiff base ligand synthesized from 4, 6-diacetylresorcinol and diethylenetriamine," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 77, no. 1, pp. 117–125, 2010.

[7] R. Hernandez-Molina and A. i Mederos, "Acyclic and macrocyclic Schiff base ligands," *ChemInform*, vol. 35, no. 48, p. no-no, 2004.

[8] G. G. Mohamed, H. F. A. El-Halim, M. M. El-Dessouky, and W. H. Mahmoud, "Synthesis and characterization of mixed ligand complexes of lomefloxacin drug and glycine with transition metals. Antibacterial, antifungal and cytotoxicity studies," *Journal of Molecular Structure*, vol. 999, no. 1–3, pp. 29–38, 2011.

[9] Z. H. Chohan, A. Munawar, and C. T. Supuran, "Transition metal ion complexes of Schiff-bases. Synthesis, characterization and antibacterial properties," *Metal-based drugs*, vol. 8, no. 3, pp. 137–143, 2001.

[10] V. Stilinović, D. Cinčić, M. Zbačnik, and B. Kaitner, "Controlling solvate formation of a Schiff base by combining mechano-chemistry with solution synthesis," *Croatica Chemica Acta*, vol. 85, no. 4, pp. 485–493, 2012.

[11] M. Yusha'u and F. U. Sadisu, "Inhibition activity of detarium microcarpum extracts on some clinical bacterial isolates," *Biological and Environmental Science Journal for the tropics*, vol. 8, no. 4, pp. 113–117, 2011.

[12] S. A. Shaker, Y. F. A. Aziz, and A. A. Salleh, "Synthesis and Characterization of Mixed Ligand Complexes of 8-Hydroxyquinoline and o-hydroxybenzylidene-1-phenyl-2, 3-dimethyl-4-amino-3-pyrazolin-5-on with Fe (II), Co (II), Ni (II) and Cu (II) ions," *European journal of scientific research*, vol. 33, no. 4, pp. 702–709, 2009.

[13] S. A. Carabineiro *et al.*, "Synthesis and characterization of tetrahedral and square planar bis (iminopyrrolyl) complexes of cobalt (II)," *Inorganic chemistry*, vol. 46, no. 17, pp. 6880–6890, 2007.

[14] R. J. Fitzgerald and G. R. Brubaker, "Contact shift studies of the square-planar complex bis (dithioacetylacetonato) cobalt (II)," *Inorganic Chemistry*, vol. 8, no. 11, pp. 2265–2267, 1969.

[15] S. Sani and I. T. Siraj, "Copper (II) and Zinc (II) Complexes Synthesized by Green Mechanochemical

Method and their Antimicrobial Studies," *Communication in Physical Sciences*, vol. 7, no. 2, 2021.

[16] S. B. Kalia, K. Lumba, G. Kaushal, and M. Sharma, "Magnetic and spectral studies on cobalt (II) chelates of a dithiocarbazate derived from isoniazid," 2007.

[17] S. Quaresma, V. André, A. Fernandes, and M. T. Duarte, "Mechanochemistry–a green synthetic methodology leading to metallodrugs, metallopharmaceuticals and bio-inspired metal-organic frameworks," *Inorganica Chimica Acta*, vol. 455, pp. 309–318, 2017.

[18] S. Sani, M. A. Kurawa, and I. T. Siraj, "Solid State Synthesis, Spectroscopic and X-ray Studies of Cu (II) Schiff base Complex Derived from 2-Hydroxy-3-methoxybenzaldehyde and 1, 3-Phenylenediamine," *ChemSearch Journal*, vol. 9, no. 1, pp. 76–82, 2018.

[19] K. Nakamoto, "Infrared and R aman Spectra of Inorganic and Coordination Compounds," *Handbook of Vibrational Spectroscopy*, 2006.

[20] W. Zhong, G. Q. Zhong, Y. Zhang, and Q. Zhong, "Solvent-Free Synthesis and Characterization of the Zn (II) Complexes with Amino Acid Schiff Base," in *Advanced Materials Research*, 2012, vol. 455, pp. 740–745.

[21] R. S. Joseyphus and M. S. Nair, "Synthesis, characterization and biological studies of some Co (II), Ni (II) and Cu (II) complexes derived from indole-3-carboxaldehyde and glycylglycine as Schiff base ligand," *Arabian Journal of Chemistry*, vol. 3, no. 4, pp. 195–204, 2010.

[22] H. S. Saleem, B. A. El-Shetary, and S. M. Khalil, ""Potentiometric and Spectrophotometric Studies of Complexation of Schiff base Hydrazine containing the pyrimidine moity," *J. Serb. Chem. Soc*, vol. 68, no. 10, pp. 729–748, 2003.

[23] R. Zaky and A. Fekri, "Solvent-free mechanochemical synthesis of Zn (II), Cd (II), and Cu (II) complexes with 1-(4-methoxyphenyl)-4-(2-(1-(pyridin-2-yl) ethylidene) hydrazinyl)-1H-pyrrole-3-carbonitrile," *Green Processing and Synthesis*, vol. 7, no. 6, pp. 515–523, 2018.

[24] J. Zhou, L. Wang, J. Wang, and N. Tang, "Antioxidative and anti-tumour activities of solid quercetin metal (II) complexes," *Transition Metal Chemistry*, vol. 26, no. 1, pp. 57–63, 2001.

[25] E. G. Ferrer *et al.*, "Synthesis, characterization, antitumoral and osteogenic activities of quercetin vanadyl (IV) complexes," *JBIC Journal of Biological Inorganic Chemistry*, vol. 11, no. 6, pp. 791–801, 2006.

[26] W.-K. Dong, Y.-X. Sun, C.-Y. Zhao, X.-Y. Dong, and L. Xu, "Synthesis, structure and properties of supramolecular MnII, CoII, NiII and ZnII complexes containing Salen-type bisoxime ligands," *Polyhedron*, vol. 29, no. 9, pp. 2087–2097, 2010.

[27] G. T. Tigineh and L.-K. Liu, "Studies on Mechanochemistry: Solid Coordination Compounds from Primary Aromatic Amines and Cobalt (II) Chloride Hexahydrate," *Journal of the Chinese Chemical Society*, vol. 61, no. 11, pp. 1180–1187, 2014.

[28] G. Bringmann *et al.*, "Ancistrotanzanine C and Related 5, 1 '-and 7, 3 '-Coupled Naphthylisoquinoline Alkaloids from Ancistrocladus t anzaniensis," *Journal of natural products*, vol. 67, no. 5, pp. 743–748, 2004.

[29] Z. Guo *et al.*, "Antifungal properties of Schiff bases of chitosan, N-substituted chitosan and quaternized chitosan," *Carbohydrate Research*, vol. 342, no. 10, pp. 1329–1332, 2007.

[30] A. O. de Souza *et al.*, "Antimycobacterial and cytotoxicity activity of synthetic and natural compounds," *Química Nova*, vol. 30, no. 7, pp. 1563–1566, 2007.

[31] N. Nishat, S. Hasnain, T. Ahmad, and A. Parveen, "Synthesis, characterization, and biological evaluation of new polyester containing Schiff base metal complexes," *Journal of thermal analysis and calorimetry*, vol. 105, no. 3, pp. 969–979, 2011.

AUTHORS

First Author - Ibrahim Ado, B.Sc, M.Sc. Bayero University Kano, P.M.B 3011, Kano, Nigeria. adobichiibrahim@gmail.com

Second Author - Junaidu Na'aliya, Ph.D. Bayero University Kano, P.M.B 3011, Kano, Nigeria.

Third Author – Mustapha Muhammad Haleelu, M.Sc, Federal University Dutsanma Katsina, Nigeria.

Fourth Author – Salihu Sani, Ph.D. Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria.

Correspondence Author - Ibrahim Ado, adobichiibrahim@gmail.com, +2348038931922