UJPICR Volume 2 Number 1 : June, 2022

UMYU Journal of Pure and Industrial Chemical Research
Volume 2 No. 1 June, 2022.
ISSN: **2814 – 1628/2814 - 1636**
DOI: https://doi.org/10.55688/ujpicr21.018

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF SOME TRANSITION METAL COMPLEXES WITH 1-PHENYLBUTANE-1,3-DIONE AND ETHYLENEDIAMINE

***Sulaiman Sani Yusuf[1], Muhammadu Marwana Yusuf[1] and Muhammad Saleh Salga[1]**
[1]Department of Pure and Industrial Chemistry, Faculty of Natural and Applied
Sciences, Umaru Musa Yar'adua University, Katsina, P. M. B 2218, Katsina State,
Nigeria.
Corresponding Author: ssmahuta01@yahoo.com

Abstract:

In this study, tetraaza macrocyclic ligand was prepared by condensation of 1-phenylbutane-1,3-dione and ethylenediamine in ethanol. Its metal (II) complexes were synthesized from the chloride salts of Cd(II), Co(II), Cu(II), Ni(II) and Zn(II). The compounds were characterized on the basis of solubility, melting/decomposition temperatures, FT-IR, molar conductance and magnetic moments. The antibacterial activity of all synthesized compounds has been evaluated against *Staphylococcus aureus* and *Escherichia coli* using agar cup-plate method. The FT-IR spectra of the ligand showed band at 1655cm^{-1} due to azomethine which confirms the formation of the ligand. This peak shifted towards the lower frequencies of 1628cm^{-1}, 1596cm^{-1}, 1611cm^{-1}, 1600cm^{-1} and 1600cm^{-1} in the spectra of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) complexes respectively which is attributed to the binding of the nitrogen of azomethine to the metal ions. The ligand and its complexes were found to be active against both *Staphylococcus aureus* and *Escherichia coli*.

Keywords: Ligand, Macrocyclic, Complexes, Characterization, Antibacterial

Introduction

The field of coordination chemistry is one of the most attractive and experimentally demanding frontiers in modern chemical sciences. It has grown from a readily defined and limited area into the most active research field of inorganic chemistry [1]. Schiff bases are condensation products of primary amine and an aldehyde or ketone. The carboxyl group of the aldehyde gives aldimines while ketone gives ketoimines [2].

Schiff base represent one of the most classes of ligands in coordination chemistry due to their convenient synthetic preparation and high versatility. These aspects influence their ability to form stable complexes with majority of transition metal ions [3]. A number of Schiff bases containing the amino functionality have been shown to have a wide range of biological activities, including antibacterial, antifungal, antidiabetic, antitumor, antiproliferative, anticancer, anticorrosive and anti-inflammatory activities [4-7]. It is believed that the biological activity is related to the hydrogen bonding through the imino group of Schiff bases with the active centres of the cell constituents [8].

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists in recent years because of its importance in the area of coordination chemistry. The family of complexes with aza-macrocyclic ligands has remained a focus of scientific attention for many decades [9].

The macrocyclic Schiff base ligands have received vital attention not only because of their pharmacological properties like antifungal, anticancer, antiviral, antibacterial character [10, 11] and their mixed soft-hard donor character, versatile coordination behaviour [12], but also for their capacity for chemical recognition of anions and metals of biochemical, medical and environmental importance [13]. They are able to form stable and selective complexes with a variety of inorganic and organic cations, and by reaction with some anionic and neutral organic and biological substrates give supramolecular compounds with specific properties and applications [14].

Recently, these macrocyclic compounds have been applied as photo conducting agents in photocopiers, laser printers, and optical read/write disks. They are expected to play a more versatile role in material chemistry due to their potential applications in molecular electronics and phototonics, electrochromic displays, nonlinear optics, electro catalytic reagents, and medical applications [15].

Due to this growing research interest in the macrocyclic complexes, this work/article concentrate on the synthesis, characterization and antibacterial studies of 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraeneLigand and its complexes of cadmium(II), cobalt(II), copper(II), nickel(II) and zinc(II)

Experimental

Materials

All the chemicals used were of analytical grade, procured from Qualikems and used without further purifications. Melting point/decomposition temperature ware determined using IA9000 series digital melting point apparatus while conductivity measurements were conducted using HI-2300 conductivity meter. IR measurements were recorded using Agilent Technologies carry 630FT-IR spectrometer at the range of 4000-400cm^{-1}. The magnetic moments of the complexes were determined on MSB MKI at 25^{o}C. All laboratory works were carried out October, 2017 to March, 2018 at Department of Pure and Industrial Chemistry Post-graduate laboratory, Umaru Musa Yarádua University Katsina, Nigeria and Chemistry Department Research Laboratory, Bayero University Kano, Nigeria.

Preparation of the Ligand (L)

A hot ethanolic solution (20ml) of 1-phenylbutane-1,3-dione (3.23g, 0.02mol) and ethanolic solution of ethylenediamine (1.20g, 0.02mol) were mixed with constant stirring. The mixture was refluxed at 80-85°C for 6 hours in the presence of few drops of HCl (pH~3-4). The resulting solution was kept overnight at room temperature. The precipitate formed was separated out, filtered, washed and recrystallized with methanol/ethanol (60:40) and dried over P_4O_{10} in vacuum [16].

Synthesis of metal complexes

An ethanolic solution (20ml) of the corresponding metal salts (0.001mol) and a hot ethanolic solution (20ml) of the ligand (0.50g, 0.001mol) were mixed together with constant stirring. The reaction mixture was refluxed for 4 hours at 80-85°C. The corresponding product(s) formed were cooled, filtered, washed and recrystallized with methanol/ethanol (60:40) and dried over P_4O_{10} in vacuum.

Conductivity Measurements

Few grams of the complexes were dissolved in 10ml of the solvent (DMSO). The molar conductance measurements of the complexes were carried out at room temperature and are recorded using conductivity meter. The results obtained are shown in table 3

Determination of Ligand to Metal ratio by Job’s method

The ligand to metal ratio in the complexes was determined using a spectrophotometer. The solution of the ligand (0.003M), the solution of metal ions (0.003M) and Nitric acid solution (0.5M) were mixed systematically, forming ten solution mixtures containing various volumes of the three solutions. The absorbance of the ten solution mixtures was taken at a wavelength of maximum absorbance [17]. The results obtained were shown in table 4. The number of coordinated ligand(s) per metal ion **(n)** was calculated using the expression below;

$$\tilde{n} = \frac{\mathbf{X}\boldsymbol{i}}{\mathbf{1 - X}\boldsymbol{i}}$$

Key:

ñ = average number of coordinated ligand per metal ion

Xi = Mole fraction

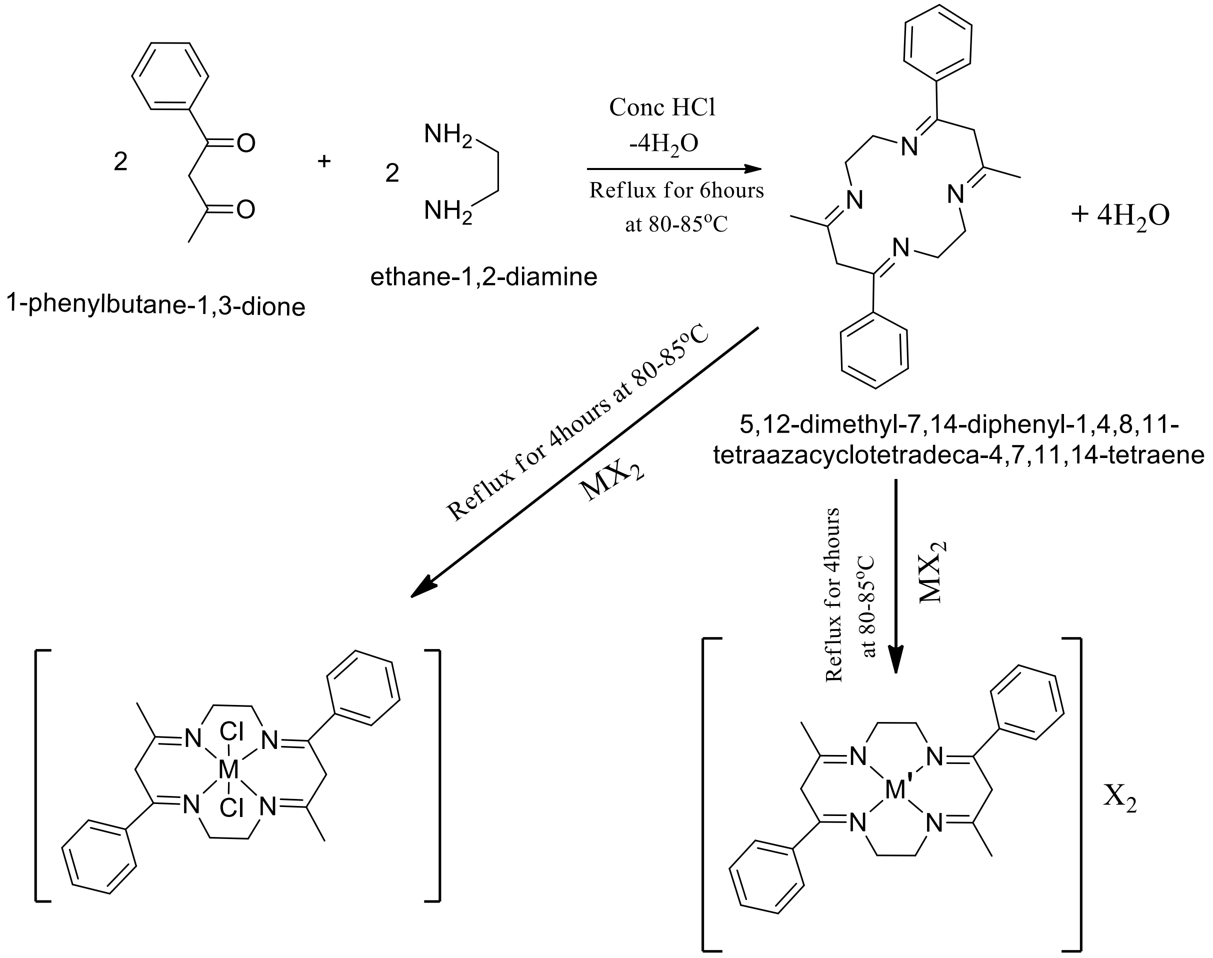
Fourier Transform Infrared Spectroscopy Analysis (FT-IR)

FT-IR analysis was carried out at Bayero University Kano, Nigeria using Agilent Technologies carry 630 FT-IR spectrometer. A small amount of the sample was placed on the FT-IR spectrometer. The spectrometer directs beams of IR at the sample and the frequencies at which the sample absorbs the infrared light were measured.

Antibacterial screening

The ligand and its metal complexes were screened for antibacterial activity against *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) using agar cup-plate method. The suspension of each microorganism was rubbed onto the surface of solidified Muller Hinton agar (Hi-Media) already poured into Petri dishes. Different concentrations (50000µg/ml, 5000µg/ml and 500µg/ml) of the ligands and the metal complexes in DMSO were prepared through serial dilution and placed on the culture media before incubation at 37°C for 24 hours. Ciprofloxacin in DMSO was used as reference standard for positive control whereas distilled water was used as negative control. The zone of inhibitions was measured and recorded as shown in table 6.

Scheme of the reaction



Where M= Cd(II) and Zn(II), M'= Co(II), Cu(II), and Ni(II), X=chloride ions

Scheme 1: Synthesis of ligand and its metal complexes

Results and Discussions

Physical data of the synthesized ligand and its complexes

The condensation of 1-phenylbutane-1,3-dione and ethylenediamine yields 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraeneLigand (72%). The metal (II) complexes were obtained by refluxing the ligand and the metal chlorides as shown in the scheme of the reaction (Scheme 1). The ligand is creamy in colour while the complexes appeared to have off-white, pink, greenish blue, light green and milk colours for Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) complexes respectively (table 1). The colour of the ligands can be attributed to the presence of the chromophore (C=N) in its structure while that of the complexes is assignable to the charge transfer and various electron transitions [18]. The ligand melts at a temperature of 154°C, while its metal complexes decomposed at temperatures of 264°C, 287°C, 211°C, 192°C and 244°C for Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) complexes respectively (table 1) and it indicates possible coordination of the various metals used and high thermal stabilities of the compounds [19].

Table 1: Physical data of the synthesized ligand and its complexes

S/N	COMPOUND	COLOUR	YIELD (%)	M.P/D.T (^{0}C)	MOL. WT. (calcd.)
1	($C_{24}H_{28}N_4$)	Creamy	72	154	372.51
2	$[Cd(L)]Cl_2$	Off-White	74	264	555.82
3	$[Co(L)Cl_2]$	Pink	78	287	502.35
4	$[Cu(L)Cl_2]$	Greenish Blue	69	211	506.96
5	$[Ni(L)Cl_2]$	Light Green	67	192	502.11
6	$[Zn(L)]Cl_2$	Milk	70	244	508.79

Where L= $C_{24}H_{28}N_4$

Solubility test of the ligand and its metal (II) complexes

The solubility test (Table 2) showed that the ligand and its metal complexes exhibit different behaviour in some common solvents. Some of the compounds were found to be soluble in methanol and ethanol while some were slightly soluble. The ligand and its metal complexes are completely soluble in dimethylsulphoxide (DMSO) which may be due to the high dielectric constant of the solvent [3].

Table 2: Solubility test of the ligand and its metal (II) complexes in some common solvents

S/N	Compound	Acetone	Chloroform	Ethanol	Methanol	DMSO	Distilled water
1	($C_{24}H_{28}N_4$)	S	S	SS	SS	S	IS
2	$[Cd(L)]Cl_2$	S	SS	S	S	S	IS
3	$[Co(L)Cl_2]$	SS	IS	SS	S	S	IS
4	$[Cu(L)Cl_2]$	SS	IS	SS	SS	S	IS
5	$[Ni(L)Cl_2]$	SS	IS	S	S	S	IS
6	$[Zn(L)]Cl_2$	S	SS	S	S	S	IS

Where L= $C_{24}H_{28}N_4$

Magnetic moment and molar conductance of the synthesized complexes

At room temperature, the Co(II), Cu(II) and Ni(II) complexes showed magnetic moments of 3.87, 1.73 and 2.83 corresponding to the 3, 1 and 2 unpaired electrons respectively, while the Cd(II) and Zn(II) complexes are diamagnetic [16, 20]. as shown in table 3. The molar conductance values of the Cd(II) and Zn(II) complexes in DMSO lies in the range 220-259$\Omega^{-1}cm^2mole^{-1}$ indicating 1:2 electrolytic natures [21, 22]. However, the molar conductance values for the rest of the complexes falls within the range 113-132$\Omega^{-1}cm^2mole^{-1}$ [9] as shown in table 3. An octahedral geometry has been proposed for the Co(II), Cu(II) and Ni(II) complexes whereas square planar geometry has been proposed for the Cd(II) and Zn(II) complexes.

Table 3: Magnetic moment and molar conductance of the synthesized complexes

S/N	COMPOUND	MOLECULAR FORMULA	μ_{eff} (B.M)	MOLAR CONDUCTANCE ($\Omega^{-1}cm^2mole^{-1}$)
1	$[Cd(L)]Cl_2$	$C_{24}H_{28}CdN_4Cl_2$	Diamagnetic	259
2	$[Co(L)Cl_2]$	$C_{24}H_{28}CoN_4Cl_2$	3.87	113
3	$[Cu(L)Cl_2]$	$C_{24}H_{28}CuN_4Cl_2$	1.73	115
4	$[Ni(L)Cl_2]$	$C_{24}H_{28}NiN_4Cl_2$	2.83	132
5	$[Zn(L)]Cl_2$	$C_{24}H_{28}ZnN_4Cl_2$	Diamagnetic	220

Where L= $C_{24}H_{28}N_4$

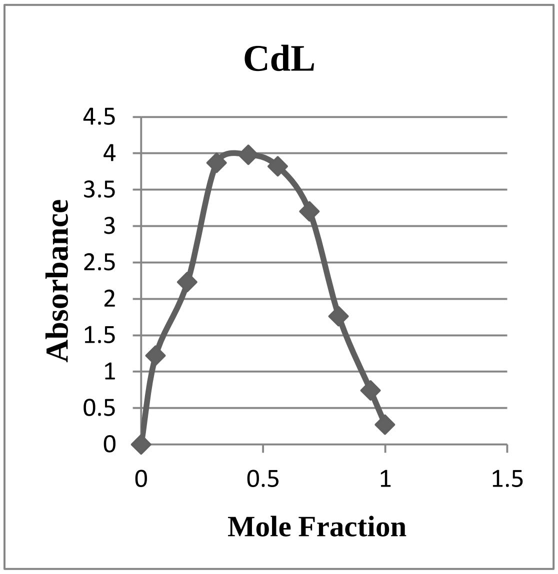
Job's Method Analysis

Job's method of continuous variation was used for the estimation of the ligand to metal ratio [17]. The plot of absorbance against mole fraction in each case at maximum absorbance corresponding to the ligand mole fraction suggest 1:1 metal-ligand ratio in the complexes [23] as shown in table 4 and Figures 1-5. Thus these complexes may be formulated as $[M(L)]X_2$ and $[M'(L)X_2]$ [16] where M=Co(II), Cu(II) and Ni(II), M'= Cd(II) and Zn(II), L= ligand, while X=Cl.

Table 4: Job's Method Data

Mole fractions, X		1.00	0.94	0.81	0.69	0.56	0.44	0.31	0.19	0.06	0.00
S/N	COMPOUND	Absorbance at λmax (nm)									
1	$[Cd(L)]Cl_2$	0.27	0.74	1.76	3.20	3.82	3.98	3.87	2.23	1.22	0.01
2	$[Co(L)Cl_2]$	0.35	0.79	1.69	2.53	3.54	3.54	3.33	2.16	1.10	0.01
3	$[Cu(L)Cl_2]$	0.29	0.76	1.78	3.14	3.89	4.05	3.39	2.38	1.27	0.02
4	$[Ni(L)Cl_2]$	0.36	0.81	1.72	2.76	3.83	3.94	3.35	2.17	1.12	0.02
5	$[Zn(L)]Cl_2$	0.32	0.83	1.85	2.71	3.45	3.80	3.30	2.14	1.13	0.01

Where L= $C_{24}H_{28}N_4$



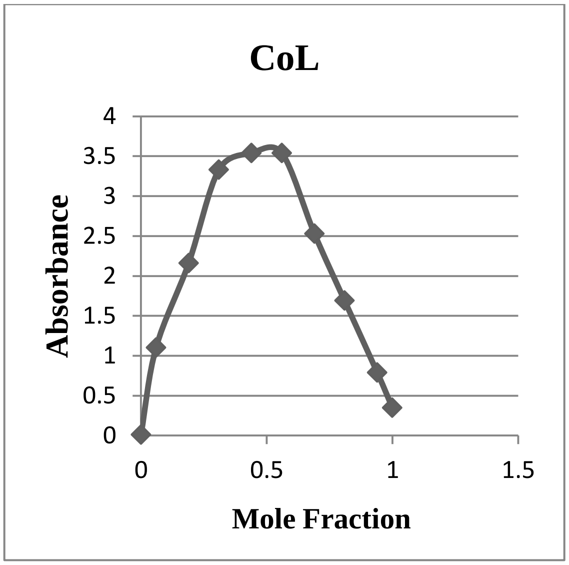
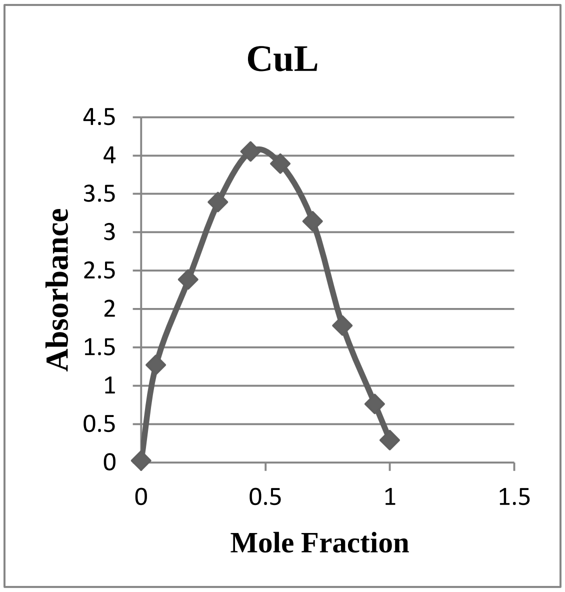


Figure 1: Job's plot of Cd Complex

Figure 2: Job's plot of Co Complex



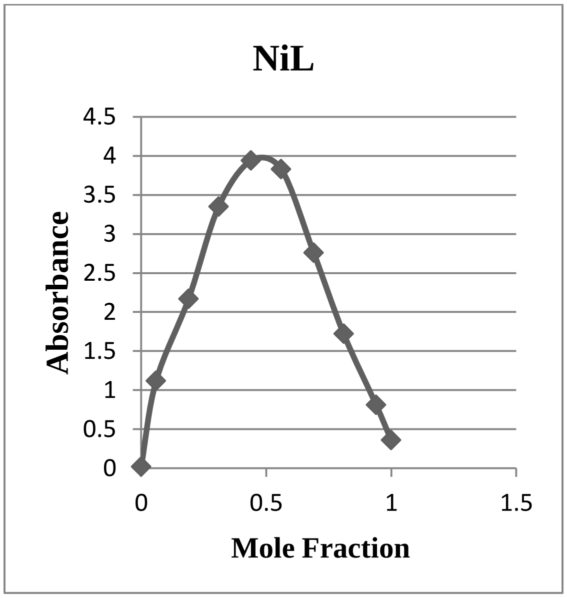


Figure 3: Job's plot of Cu Complex

Figure 4: Job's plot of Ni Complex

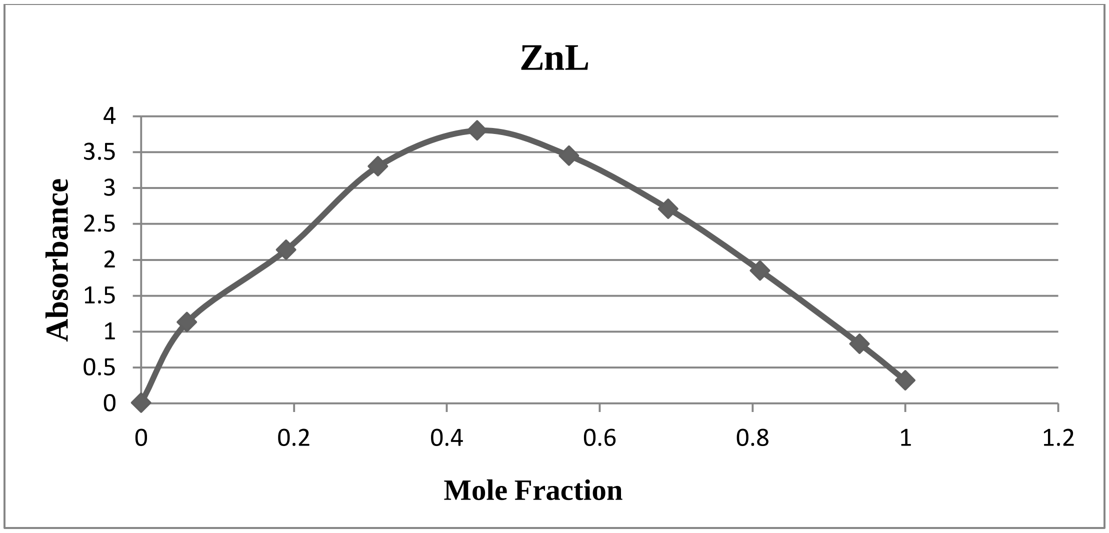


Figure 5: Job’s plot of Zn Complex

Infrared Absorption Frequencies (cm^{-1}) of the Ligand and its Metal Complexes

The important IR bands and their assignment in the ligand and its complexes are shown in table 5. The IR spectrum of the ligand does not exhibit any band corresponding to a free primary diamine or a free keto group which suggest the complete condensation of the amino groups with the keto groups. The ligand showed absorption peak at 1655cm^{-1} that is assignable to azomethine and confirms the formation of the ligand. On complexation, the peak shifted towards the lower frequencies 1628cm^{-1}, 1596cm^{-1}, 1611cm^{-1}, 1600cm^{-1} and 1600cm^{-1} for Cd(II), Co(II), Cu(II), Ni(II), Zn(II) complexes respectively which indicates that the nitrogen atoms of azomethine groups are coordinated to the metal ions [24]. The absorption peaks at 426cm^{-1}, 419cm^{-1},411cm^{-1},418cm^{-1} and 409cm^{-1}can be assigned to υ(M-N) for Cd(II), Co(II), Cu(II), Ni(II), Zn(II) complexes respectively [9].

Antibacterial screening of the ligand and its complexes

The synthesized compounds were also tested for their antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* using agar cup-plate method at three different concentrations. The results are listed in table 6 as determined by measuring the zone of inhibition (mm) [25]. The result showed that the Cd(II) complex has highest zone of inhibition (42mm) at the concentration of 50,000µg/ml while Cu(II) and Zn(II) complexes showed the lowest zone of inhibitions (32mm) at the same concentration against *Echericha coli*. The ligand was also found to be active against both *Staphylococcus aureus* and *Echerichia coli* though most of its complexes displayed enhanced activity. This was ascribed to the presence of metal ions in the lattice which makes it more powerful and effective bactericidal agents [26].

Table 5: Infrared Absorption Frequencies (cm^{-1}) of the Ligand and its Metal Complexes

S/N	COMPOUND	ASSIGNMENTS	
		υ (C=N)	υ (M-N)
1	($C_{24}H_{28}N_4$)	1655	-
2	[Cd(L)]Cl_2	1628	426
3	[Co(L)Cl_2]	1596	419
4	[Cu(L)Cl_2]	1611	411
5	[Ni(L)Cl_2]	1600	418
6	[Zn(L)]Cl_2	1600	409

Where L= $C_{24}H_{28}N_4$

Table 6: Infrared Absorption Frequencies (cm^{-1}) of the Ligand and its Metal Complexes

Compounds	Concentrations and zone(s) of Inhibition					
	50,000µg/ml		5,000µg/ml		500µg/ml	
	S. Aureus	*E. Coli*	*S. Aureus*	*E. Coli*	*S.Aureus*	*E. Coli*
($C_{24}H_{28}N_4$)	23mm	24mm	19mm	22mm	16mm	10mm
[Cd(L)]Cl_2	35mm	42mm	22mm	32mm	16mm	22mm
[Co(L)Cl_2]	26mm	33mm	19mm	22mm	14mm	16mm
[Cu(L)Cl_2]	25mm	32mm	23mm	28mm	15mm	20mm
[Ni(L)Cl_2]	32mm	36mm	23mm	20mm	14mm	10mm
[Zn(L)]Cl_2	30mm	32mm	21mm	24mm	16mm	16mm
Ciproflaxacin (+)	48mm	43mm	-	-	-	-
Distilled water (-)	NA	NA	NA	NA	NA	NA

Where L= $C_{24}H_{28}N_4$

NA = No Activity

It is recommended that ^{1}HNMR, ^{13}CNMR, Crystallography and mass spectroscopic analyses to be carried out. Other biological activities such as antiviral and antifungal screening of the compounds are also recommended to broaden their biological application

Table 6: Antibacterial screening of the ligand and its complexes

Conclusion

The ligand acts in a tetradentate manner coordinating through the four nitrogen atoms of the azomethine groups. An octahedral geometry has been proposed for the Co(II), Cu(II) and Ni(II) complexes, whereas square planar for the Cd(II) and Zn(II) complexes. Moreover, the antibacterial data revealed that the ligand was also found to be active against both *Staphylococcus aureus* and *Escherichia coli* though most of its complexes displayed enhanced activity as complexation tends to make the ligands acts more powerful and effective bactericidal agents.

References

1. Chandra, S., and Kumar, S.A. (2009): Nickel(II) and Copper(II) complexes with Schiff base ligand 2, 6-diacetylpyridine bis (carbohydrazone): synthesis and IR,mass, 1H NMR, electronic and EPR spectral studies. *SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy* **72 (4)**, 851-857.
2. Aliyu, H.N. and Adamu H. (2009): synthesis and characterization of n-(-i- morpholinobenzyl) semicarbazide Manganese (II) and Iron (II) Complexes. *Bayero Journal of pure and applied Sciences*. 2 (**2**), 143-148
3. Sani U. and Baba M.A. (2016): synthesis, characterization, antimicrobial and antioxidant studies of 2-[(2-hydroxyphenyl) methylidene]hydrazine-1-carboxamide and its metal (II) complexes. *Bayero Journal of pure and applied sciences*. **9** (1), 206-212. http://dx.doi.org/10.4314/bajopas.v9i1.32
4. Tarafder, M.T. H., Ali, M.A., Wee, D.J., Azahari, K., Silong, S., and Crowse, K,A. (2000): Complexes of a tridentate ONS Schiff Base, Synthesis and biological properties. *Transition Metal chemistry*. **25**, 456-460
5. Shivakumar, K., Shashidar, P., VithalReddy, P., and Halli, M.B. (2008): Synthesis, spectral, characterization and biological activity of benzofuran Schiff Bases

with Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) complexes. *Journal of Coordination Chemistry*. **61**, 2274-2287

6. Hunashal, R.D., and Satyanarayana, D. (2012): One pot synthesis of 3-(substituted phenoxymethyl)-6-phenyl/substituted phenoxymethyl-1,2,4-triazolo[3,4-b] [1,3,4] thiadiazolederavatives as antimicrobial agent. *International Journal of Pharmaceutical and Biological Sciences*. **3**, 183-192
7. Gomathi, V., and Selvameena, R. (2013): Synthesis, Characterization and biological studies of complexes of 3D transition metals and with Schiff base derived from sulfadiazine and 2-acetylnaphthalene. *International Journal of Recent Scientific Research*. **4**, pp 94-97.
8. Dharamraj, N., Viswanathanmurthi, P., and Natarajan, K. (2001): Ruthenium (II) complexes containing bidentate Schiff bases and their antifungal activity.*Transition Metal chemistry*. Volume **26**, 105-109
9. Singh D.P., Grover V., Kumar K., and Jain K. (2010): Metal ion prompted macrocyclic complexes derived from indole-2,3-dione (isatin) and O-phenylenediamine with their spectroscopic and antibacterial studies. *ActaChimicaSlovenica*. **57**, 775-780
10. Sheikh, R.A., Shreaz, S., Khan, L.A., Hashmi, A.A. (2010): Development and characterization of bioactive macrocyclic metal complexes, use as a potential drug. *J. Chem. Pharm. Res.*, **2** 172-185.
11. Shiekh, R.A., Rahman, I.A., Malik, M.A., Masudi, S.M and Luddin, N. (2012): Synthesis, spectral, electrochemical and biological studies of nitrogen donor macrocyclic ligand and its transition metal complexes. *Int. J. Electrochem. Sci.*, **7**, 12829- 12845.
12. Sengupta, P., Dinda, R., Ghosh, R., and Sheldrick, W.S. (2003): Synthesis and characterization of some biologically active ruthenium (II)complexes of thiosemicarbazones of pyridine 2-aldehyde and thiophene 2-aldehyde involving some ring substituted 4-phenylthiosemicarbazide. *polyhedron*, **22**(3), 477-453.
13. Ahmad S.R, Rahman, I.A, Malik, M.A, Luddin, N., Masudi, S.M. and Al-Thabaiti, S.A. (2013): Transition Metal Complexes with Mixed Nitrogen-Sulphur (N-S) Donor Macrocyclic Schiff Base Ligand: Synthesis, Spectral, Electrochemical and Antimicrobial Studies. *Int. J. Electrochem. Sci.,***8**(2013) 6972 – 6987
14. Bozic, L. T., Marotta, E. and Traldi P. (2007): Efficient solid-state microwave-promoted complexation of a mixed dioxa-diaza macrocycle of a sodium ethyl 4-benzeneazophosphonate complex. *Polyhedron*, **26**, 1663-1668.
15. Ertem, B., Bilgin, A., Gok Y., and Kantekin, H. (2008): The synthesis and characterization of novel metal-free and metallophthalocyanines bearing eight 16- membered macrocycles. *Dyes and Pigments*, **77**, 537-544.
16. Tyagi, M., Chandra, S., and Choudhary, S.K. (2011): Tetraaza macrocyclic complexes: Synthesis,

spectral and antifungal studies. *Journal of chemical and pharmaceutical research*. **3** (1): 56-63. Available online www.jocpr.com

17. MacKinnon, C. D. (2014): Spectroscopic Determination of a complex Ion's stoichiometry by Job's Method. *Inorganic Chemistry I LaboratoryManual(Chemistry 2351).*
18. Rodgers, G. E. (1994). Introduction to Coordination, Solid state and descriptive Inorganic Chemistry. *Mc Graw-Hill: New York*, pp 4
19. Salga, M.S and Yusuf, S.S (2017). Synthesis, characterization and antibacterial studies of tetraazamocrocyclic ligand and its Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) complexes. *Dujopas* **3**(1): 501-508
20. Nadia E.Y, Thahira Begum S. A. R., Edward R.T.T., Abhimanyu V., Karen A. C., Mohamed I.M.T., and Haslina A. (2015): Synthesis, Characterization and Biological Evaluation ofTransition Metal Complexes Derived from N, S Bidentate Ligands *Int. J. Mol. Sci.*, **16**,11034-11054; doi:10.3390/ijms160511034
21. Chandra, S., Tyagi, M., and Agrawal, S., (2010): Synthesis and characterization of a tetraaza macrocyclic ligand and its cobalt (II), nickel (II) and copper (II) complexes. *Journal of Serbian Chemical Soceity*. ***75*** (7) 935–941 UDC546. 732'742'562.004.12:547.455.4 *JSCS–4019*
22. Dharmpal S., and Kumar K., (2010): Macrocyclic complexes: synthesis and characterization. *Journal of the Serbian Chemical Soceity*. **75** *(4), 475-482*
23. Sani, S.Y., Saleh, M. S., and Sani, M.(2018):Synthesis, characterization and antibacterial studies of macrocyclic Schiff base derived from Malonic acid and o-phenylenediamine and its Cd (II), Co (II), Cu (II), Ni (II), and Zn (II) complexes *Science World Journal* Vol **13**(No 4), 65-68
24. Kalsi, P.S. (1999): Spectroscopy of organic compounds, New delhi (India); *New age international publishers*
25. Ahmad, R., S., Ismail A., Ahmad M. M., Luddin, N., Malik S. M., Ahmed S. A. (2013): Transition Metal Complexes with Mixed Nitrogen-Sulphur (N-S) Donor Macrocyclic Schiff Base Ligand: Synthesis, Spectral, Electrochemical and Antimicrobial Studies *Int. J. Electrochem. Sci.*, vol **8,** 6972 – 6987
26. Morad, F. M., Ei-ajaily, M. M., Gweirif, S. (2007): Preparation, physical characterization and antibacterial activity of Ni (II) Schiff Base complex. *Journal of Science and its Application*, **1**, 72-75