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Sythesis, Physico-Chemical and Antimicrobial Evaluation of Cu(II), Fe(II), Mn(II) Complexes with Schiff Base Derived from N-(2-hydroxybenzylidene)-3-(benzylideneamino)benzenesulfonamide

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ABSTRACT
A Schiff-base derived from N-(2-hydroxybenzylidene)-3-(benzylideneamino)benzene sulfonamide, and its metal complexes of Cu(II), Fe(II) and Mn(II) were synthesized and characterized based on their melting point decomposition temperature, solubility, molar conductance, magnetic moment and infrared analyses. Job's method of continuous variation revealed that all the metal complexes are in 1:1 Metal-Ligand ratio. Physical and analytical data suggested that the Schiff base act as tretradentate ligand towards metal ion via azomethine-N, deprotonated phenolic-O and S=O group of sulphanilamine. All the complexes have low molar conductance value (11.28-66.8$\Omega^{-1}cm^2mol^{-1}$), indicating that they are non-electrolyte. The magnetic moment values ranges from1.74 to 5.98B.M shows that all the complexes are paramagnetic in nature. The synthesized ligand and its respective metal complexes were screened for their antibacterial activity against *Staphylococcus aureus* (Gram-positive), *Escherichia coli*, (Gram-negative) bacterial strains and antifungal activity against *Mucor inducus spp* and *Aspergillus fumigatus*. The results of these studies revealed that the Schiff base and its metal complexes showed significant antibacterial and antifungal activity at high concentrations.

Keywords:

INTRODUCTION
Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds. Schiff-bases have been widely used as ligand because of the high stability of the coordination compound, of them and their good solubility in common solvents such as ethanol, methanol, chloroform, Dimethylformamide (Bharat *et al.,* 2015).

Schiff base is a compound that contains azomethine group (>C=N-) connected to an aryl or alkyl group but not hydrogen. Schiff bases can be synthesized from an amine and a carbonyl compound by nucleophilic addition forming a hemi-aminal group followed by dehydration to generate an imines compound. Schiff bases are important due to carbon nitrogen double bond (C=N) which can coordinate with metal (Uddin *et al.,* 2014).

These important compounds have been reported to possess diverse biological activities such as antifungal, analgesic, anti-inflammatory, antibacterial, antioxidant, antitumor, cardiovascular, antitubercular and as local anesthetic. (Neelofar, *et al*., 2017)

Schiff bases form an interesting class of chelating ligand that has enjoyed popular use in the coordination chemistry of transition elements. A large number of Schiff bases and their metal complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen and their use in catalyses and biological systems (Shoair *et al.,* 2015)

A number of sulphanilamine Schiff bases were the first effective chemotherapeutic agents employed systematically for the prevention and cure of bacterial infections in humans (Maria, 2003).

Schiff base metal complexes play a significant role in the development of chelation chemistry, the chelation makes these compounds effective and stereo specific catalyst for oxidation, reduction and hydrolysis, and they also show biological activity and other transformation of organic and inorganic chemistry (Kawkab and Al-Ali, 2012).

EPERIMENTAL
Apparatus

All glass wares used in this work were washed with detergent after soaking in conc. HNO_3, rinsed with distilled water and dried in an oven at 110°C. All weighing were carried out on an electric Metler balance model B154, melting point and decomposition temperature were determined using Gallenkamp melting point apparatus. Molar conductivity was determined using Jenway 4010 model conductivity meter, IR-spectral analysis was recorded on a Fourier transformed infrared spectrophotometer 8400S model.

Reagents

All chemicals used in this work were of analytical grade and were used without further purification.

Preparation of Schiff Base

The Schiff base was prepared by mixing Sulphanilamine (3.44g, 0.02mol) with salicylaldehyde (4.49g, 0.04mol) in 50cm^3 of ethanol. The resulting mixture was refluxed for one and half hrs. Upon cooling, the obtained light yellow crystalline precipitates were filtered, washed with diethyl ether and then finally dried in desiccators over $CaCl_2$.Similar to the report of Ümmühan *et al.* (2008).

Preparation of Schiff Base Metal Complexes

The metal complexes were prepared by mixing an ethanolic solution (50cm^3) of the Schiff base (0.02mol) with an ethanolic solution (50cm^3) of the metal (II) chloride (0.01mol). The resulting mixture was refluxed for one hour and left in an ice bath for 3hours. The solid complexes formed were collected by filtration, washed with a small volume of ethanol and diethyl ether, and then dried in desiccators over $CaCl_2$. Similar to the report of (Ümmühan *et al.*, 2008) .The metals salts used include Cu(II), Mn(II) and Fe(II) salts respectively.

Determination of Melting Point of the Schiff base and Decomposition Temperature of the metal complexes

Melting point of the Schiff base as well as decomposition temperature of the metal complexes were determined by introducing a pinch of each samples into a capillary tube and then inserted into Gallenkamp melting point Apparatus, the temperature at which the ligand melt and the complexes decomposed were recorded. (Aliyu and Ado, 2011)

Solubility Test

Small amount of each of the metal complexes and Schiff base was taken and transferred into test-tube containing little amount of the corresponding solvents and their solubility test were determined. The solvent used were, distilled water, ethanol, methanol, DMSO, diethyl ether, acetone, chloroform, DMF and nitrobenzene and the results are shown in Table 1 (Aliyu and Ado, 2011).

Molar Conductance Measurement

Molar conductance of the complexes were carried out in DMSO by dissolving 0.001gm of each sample in 10ml of the solvent in a test-tube, the electrode was inserted and the readings were taken. The results obtained were compared with the results reported by Aderoju *et al.* (2015).

Magnetic Susceptibility Measurement

Prepared metal complex was introduced into a capillary tube up to a given mark and the reading recorded using the magnetic susceptibility balance (Javed *et al.*, 2006).

$$Xg = \frac{C\ x\ L\ (R - R_o)}{10^9\ M}$$

Determination of Metal to Ligand Ratio

Number of the ligand coordinated to the metal ion was determined using Job's method of continuous variation (Angelici, 1971).

3.0 mmol aqueous solution of the ligand and the metal chlorides were prepared. The following quantities of Metal salt ratio (ml); 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 were taken from the ligand solution and each of the metal chloride solutions respectively. A total volume of 16ml was maintained (in that order) throughout the process and the mole fraction of the ligand was calculated in each mixture. The solutions of the metal chlorides were scanned (as blank) to find the wavelength of maximum absorption (λ_{max}) for that particular metal ion (Angelici, 1971). The machine was fixed at λ_{max} (in each case) before taking the absorbance values.

The absorbance values were plotted against mole fraction of the ligand and the number of coordinated ligand (coordination number) was determined using the relation below:

$$\bar{n} = \frac{x_i}{1-x_i}$$

Where $\bar{n}$ = number of coordinated ligand, and
x_i= mole fraction at maximum absorbance

Antibacterial Activity Test

The ligand and complexes were dissolved separately in DMSO to have three different concentrations (15µg, 30µg and 60µg) per disc. They were placed on the surface of the culture media (nutrient agar) and incubated at 37°C for 24hrs. Then in vitro antibacterial activity against *Staphylococcus aureus* (Gram-positive), *Escherichia coli* (Gram-negative) of the ligand and complexes were carried out by disc diffusion method. The diameter of zone of inhibition produced by the ligand and complexes was compared with the standards, which are 15µg, 30µg and 60µg (Bharat, *et al.*, 2015).

Antifungal Activity Test

The ligand and complexes were dissolved separately in DMSO to have three different concentrations (15µg, 30µg and 60µg) per disc. They were placed on the surface of the culture media (sabouroud dextrose agar) and incubated at room temperature for 48hrs. Then in vitro antifungal activity against *Mucor inducus spp and Aspergillus fumigatus* of the ligand and complexes were carried out by disc diffusion method. The diameter of zone of inhibition produced by the ligand and complexes was compared with the standards (15µg, 30µg and 60µg). The antimicrobial activity for the Schiff base and its metal (II) complexes were determined using disc diffusion method. The diameters of zone of inhibition (mm) were measured for both discs. The ligand showed little activity against the entire tested organism at all concentration (Ahmad *et al.*, 2016).

RESULTS AND DISCUSSIONS

Table 1: Physical Properties of the ligand and its corresponding metal (II) Complexes

Compound/Ligand	Colour	Percentage Yield(%)	Melting Point (˚C)	Decomposition Temperature(˚C)
Ligand, L′	Yellow	55.8	198	-
[FeL′]	Black	89.1	-	277
[MnL′]	Yellow	81.6	-	286
[CuL′]	Brown	86.1	-	294

Where L′ = $C_{13}H_{14}O_4N_2S$

Table 2: Molar Conductance of complexes in (1×10^{-3}M) in DMSO Solution

Complex	Concentration Moldm^{-3}	Specific Conductance Ohm^{-1}cm^{-1}	Molar conductance Ohm^{-1} cm^{2} mol^{-1}
[FeL′]	1×10^{-3}	37.8×10^{-6}	37.8
[MnL′]	1×10^{-3}	29.6×10^{-6}	29.6
[CuL′]	1×10^{-3}	40.6×10^{-6}	40.6

Where L′ = $C_{13}H_{14}O_4N_2S$

Table 3: Solubility of the Ligand and its metal (II) complexes in some common solvents

Compound	Water	Ethanol	Methanol	DMSO	Acetone	Diethyl ether	Chloroform	hexane	CCl_4
Ligand, L′	IS	SS	IS	S	S	IS	IS	SS	SS
[FeL′]	SS	SS	S	S	S	SS	IS	SS	IS
[MnL′]	SS	SS	SS	S	S	IS	IS	IS	IS
[CuL′]	IS	SS	SS	S	IS	IS	SS	IS	IS

KEY: S= Soluble, SS = Slightly Soluble, IS = Insoluble, DMSO = Dimethylsulfoxide.

Table 4: Magnetic susceptibility values of the metal (II) complexes

Complex Compound	Mass Susceptibility (Xg) (g^{-1})	Molar Susceptibility (Xm) (mol^{-1})	μ_{eff}(B.M)
[FeL′]	31.2×10^{-6}	0.010	4.89
[MnL′]	42.2×10^{-6}	0.0136	5.69
[CuL′]	3.85×10^{-6}	0.012	1.74

Where L′ = $C_{13}H_{14}O_4N_2S$

Table 5: IR Spectra of the Schiff base and its metal Complexes

Compound	V(S=O) cm^{-1}	V(C=N) cm^{-1}	V(M-O) cm^{-1}
Ligand, L′	1311	1615	-
[FeL′]	1331	1631	544
[MnL′]	1311	1615	590
[CuL’]	1309	1607	591

Where L′ = $C_{13}H_{14}O_4N_2S$

Table 6: Job’s Method Analysis

Mole fraction X(total volume=10ml	Cu:L’	Mn:L’	Fe:L’
0:10	0.041	0.02	0.06
1:09	0.06	0.028	0.09
2:08	0.085	0.03	0.12
3:07	0.101	0.036	0.13
4:06	0.111	0.04	0.142
5:05	0.128	0.049	0.190
6:04	0.101	0.039	0.150
7:03	0.090	0.036	0.12
8:02	0.052	0.025	0.1
9:01	0.038	0.020	0.082

Table: 7: Antibacterial activity of Schiff Base and Metal (II) Complexes

Test Organism/Compound Complex		**Concentration (µg)/ Zone of Inhibition (mm)**			**Control (mm)**
		60	**30**	**15**	
Staphylococcus aureus	Ligand, L′	15	8	7	Amphiclox
	[FeL′]	18	17	13	28
	[MnL′]	10	9	8	
	[CuL′]	16	15	13	
Escherichia coli	Ligand, L′	13	12	8	Amphiclox
	[FeL′]	18	15	12	22
	[MnL′]	14	12	8	
	[CuL′]	12	10	8	

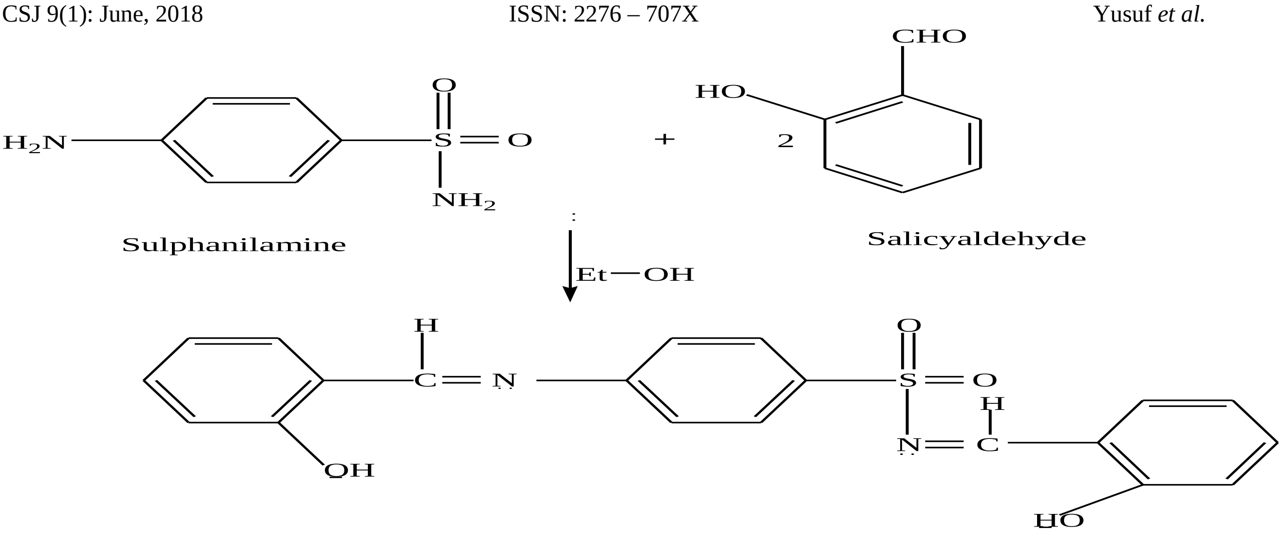
Where L′ = $C_{13}H_{14}O_4N_2$

Table: 8: Antifungal activity of Schiff Base and Metal (II) Complexes

Test Organism/Compound Complex		**Concentration (µg)/ Zone of Inhibition (mm)**			**Control (mm)**
		60	**30**	**15**	
Aspergillus formigatus	Ligand, L′	15	12	10	Grisofulvin
	[FeL′]	12	10	8	32
	[MnL]	15	13	12	
	[CuL′]	17	15	10	
Mucor spp.	Ligand, L′	20	15	14	
	[FeL′]	12	10	8	31
	[MnL′]	20	18	14	
	[CuL′]	20	18	15	

DISCUSSION

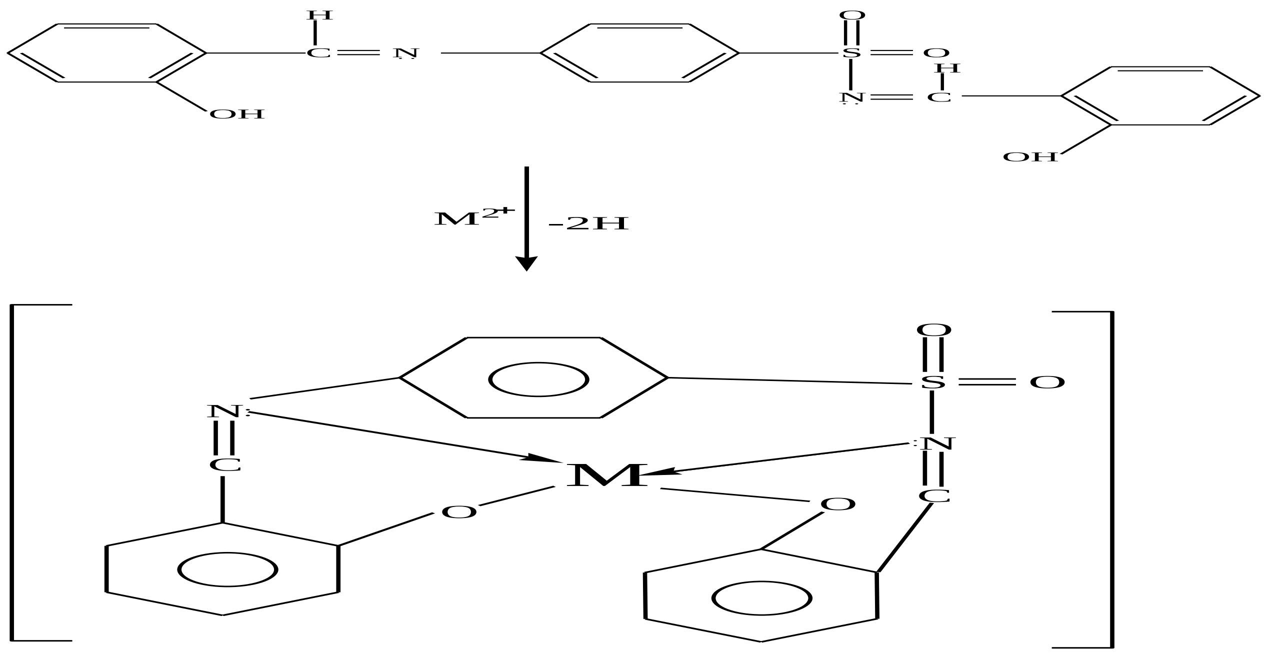
The Schiff base of salicylaldehyde was prepared as reported by a similar work of Ashraf, (2011) which was found to be yellow solid crystal. It was observed to have a modest yield of 55.8%.



Scheme 1: Preparation of Schiff base

Treatment of the prepared Schiff base with some metal (II) ions [Cu(II), Fe(II), Mn(II)] in 1:1 ratio afforded the corresponding complexes with varying color. (Table 2) All the complexes prepared have an appreciable percentage yields in the range of (81.6 – 89.1%), which are higher than yields obtained for the Schiff base ligand, (55.8). Fe(II) of the salicylaldehyde Schiff base has the highest value of 89.1% and the least was 81.6% for Cu(II) complex, which justified that Fe(II) complex has the highest percentage yield out of the all prepared metal complexes. This is in agreement with the results reported by Aliyu and Bello, (2010).

Decomposition temperatures of the complexes were found to be in the range of 277 – 294°C, their values indicates that the metal complexes are stable and are in agreement with values of similar metal (II) complexes reported by Ashraf, (2011),
Magnetic susceptibility studies indicated that complexes of Cu(II) Fe(II) and Mn(II) were paramagnetic with the values ranging from 1.74 – 5.69B.M which is in agreement with similar paramagnetic compounds reported in the literature (Anacona, *et al.,* 2015).



Scheme2: Preparation of Complexes. (Where M = Cu(II), Mn(II), Fe(II))

Solubility of ligand and the corresponding metal complexes were also determined in different solvents; the ligand was found to be soluble in acetone, but insoluble in water, while the complexes were found to be soluble in acetone and DMSO, insoluble in water, and slightly soluble in ethanol, menthol, and chloroform. The results are presented in Table 3. Similar to the results reported by Aliyu and Ado, (2011).

Molar conductance of the complexes (10^{-3}M) in DMSO were determined, the results obtained indicates values in the range of 29.6-40.6Ohm^{-1} cm^2 mol^{-1}, which is quite lower for an electrolyte. The lower values indicate few ion or absence of ions in DMSO. Therefore the results indicate non electrolytic of the complexes prepared in this work. The results are presented in Table 2. Which are in line with the report of Mustapha *et al.,* (2011).

The infrared spectral result of the Schiff base ligand showed vibrational peak at 1311cm^{-1} which may be attributed to the v(S=O) group. The bands in the range 1607cm^{-1}-1631c m^{-1} are all observable in the metal complexes prepared, which is an indication of the participation of the azomethine nitrogen in coordination to the metal ions. Also, in the spectral of the Schiff base. Now absorption bands at 760cm^{-1} and 795cm^{-1} and 544cm^{-1} and 591cm^{-1} in the metal (II) complexes indicate the formation of M-N and M-O bonds respectively. This indicates that the ligand is coordinated to the metal ions through these groups as reported by Kumar *et al.,* (2012) the results are shown in Table 5.

Estimation of the Metal to Ligand ratio was achieved by using Job's method of continuous variation, the results showing mole fraction of the Ligand and absorbance for the respective metal ions (Mn^{2+}, Fe^{2+}, and Cu^{2+}) are presented in Tables 6. (Angelici, 1971)

The plot of absorbance against mole fraction in each case gives a curve with maximum absorbance corresponding to the ligand mole fractions which were used in calculating the number of coordinated ligand, which suggest 1:1 Metal-Ligand ratio in all the prepared complexes as reported by Anacona *et al.,* (2015)

Schiff base and it's corresponding metal complexes of Fe(II), Mn(II), Cu(II), showed significant activity against all the two tested bacterial strains (*Staphylococcus aureus, Escherichia coli*) as evident from the zone of inhibition as shown in Table 7. Which is closer enough to a similar results reported by Bharat, *et al.,* (2015)

The antifungal activity studies of the compound showed that the Schiff bases are inactive against the two fungal isolates (*Aspergillus fumigatus* and *Mucor species)* even at higher concentrations. Whereas all the prepared metal complexes showed activity against the two fungal isolates. The Cu(II) complex shown highest activity against the two fungal isolates where Fe(II) complex showed the least activity. Which is closer enough to a similar results reported by Ahmad *et al.,* (2016)

CONCLUSION

The Schiff base was prepared by condensation of salicylaldehyde and sulphanilamine. Their corresponding Fe(II), Mn(II), Cu(II), complexes were also prepared from the reaction of ethanolic solution of the Schiff base and metal (II) chloride.

Characterization of the complexes indicates that, they are non-electrolytic. The decomposition temperature of the metal Schiff base revealed high values which is an indication of high stability. The solubility test carried out in various solvents, showed they are all soluble in DMSO.

IR- spectroscopy indicated the Schiff base ligand is coordinated to the central metal ions. The antimicrobial activity of the ligand and their metal complexes indicated that the metal (II) complexes were more active than the free Schiff base on one or more isolates.

REFERENCES

Aderoju A. Osowole S. Sherifah M. (2015). Synthesis, Characterization and Antimicrobial Activity of some Mixed Trimethoprim- Sulfamethoxazole Metal Drug Complexes. *World Applied Sciences Journal* 33(2); 336-342.

Ahmad S.A, Rabie S.F, Alaa E.M, and Abdel H. (2016). Synthesis, characterization and Antimicrobial Activity of Schiff base (E)-N-(4-(2-Hydroxybenzylideneamine) phenylsalfonyl) Acetamide metal complexes. *American Journal of Analytical Chemistry*, 7 PP 233-245.

Aliyu H.N and Ado I. (2011). Studies of Mn(II) and Ni(II) complexes with Schiff base derived from 2-amino benzoic acid and salicylaldehyde. *Biokemistri* 23(1): 9-16.

Aliyu H. N. and Bello I. (2010): Synthesis and Characterization of Diaquo Bis(N – Histidyl- 2, 4 - Pentanedionato) Copper (II) Complex. *Biokemistri Klobex* Academic Publishers Vol. 22, No. 2, pp 105-110.

Anacona J.R, Natiana N, Juan C. (2015). Synthesis, characterization and antibacterial activity of a tridentate Schiff base derived from ceptalothin and sulfadiazine and its transition metal complexes. *Spectrochmica Acta part A: molecules and bimolecular spectroscopy.* Vol. 137: 16-22.

Angelici, R.J. (1971): "Synthesis and Techniques in Inorganic Chemistry", W.B Savders Company, 2nd edition, pp 115-125

Ashraf, M. A., Mahmud, K., Abdul W. (2011). Synthesis characterization an Biological activity of Schiff Base. *International conference on chemistry and chemical process*, IPCBEE LACSIT, Singapore, 10: 256-264.

Bharat, A.M., Pratik, N.D., Timbadiya, P.B. (2015). Synthesis of Schiff Bases and their Transition metal Complexes characterization & application. *International Journal of Science, Technology & Management* 1(04): 642

Javed, I. (2006), Biological properties of Chloro-salicylidene Amine and Complexes with Co(II) and Cu(II). *Turk. Journal of Biochemistry,* 30(1):1-4.

Kawkab, A. and Al-Ali, H. (2010). Synthesis, characterization and study of electrical properties of Fe(III) and Al(III) of Schiff base. *Journal of inorganic chemistry* 2(3):1-11

Kumar, J. S., Priya, S., Jayachandramani, N. and Mahalashmi S. (2012). Synthesis Spectroscopic Characterization and Biological Activity of Transition Metal Complexes derived from a Tridentate Schiff Base. *Journal of Chemistry,* 21(3):1-10.

Maria, H., Torre, Gianella, F., Eduardo, K., Eduardo, E. (2003). Characterization of a Cu(II) complex of sulfadimethoxine. *Journal of Inorganic Biochemistry*. (94): 200-204.

Mustapha M., Thorat B.R., Sawant S., Atram R.G and Yamgar R. (2011). Synthesis of Novel Schiff base and its Transition Metal Complexes. *Journal of Chemical and Pharmaceutical Research* 3(4) 5-9

Neelofar, N.A., Adnan Khan, S.A., Noureen, A., Muhammad, B. (2017) Synthesis of Schiff Bases derived from 2-Hydroxy-1-naphthaldehyde and their Tin(II) Complexes for Antimicrobial and Antioxidant Activities. *Bull. Chem. Soc. Ethiop 31(3): 445-456*

Shoair, A.R., El-Shobaky, H.R., Yassin, A. (2015). Synthesis, Spectroscopic characterization, catalytic and antimicrobial studies of ruthenium (III) Schiff Base. *Journal of Molecular Liquids* (211): 217-227.

Uddin, M.N., Salam, M.A., Chowdhury, D.A. Sultana, J., Halim M.E. (2014). Trigonal Pyramidal Pb (II) Complexes of Schiff bases of Orthoaminophenol: Synthesis, Characterization and Antibacterial Evaluation. *International Journal of Advanced Research in Chemical Science* 1(6): 47-56.

Ummuhan, O., Pinar, O. Ertain, S., Fatima, H. (2007). Characterization and antibacterial activity of new sulfonamide derivates and their nickel (II), cobalt (II) complexes. *Inorganic Chimica Acta* (362): 2613 -261