



Original Research Article

Metal complexes of Co(II), Ni(II) and Zn(II) complexes of Schiff base derived from 2-aminothiophenol and 2-methoxyphenylacetaldehyde, synthesized, characterized and their microbial activity

Ishaq Yahaya Lawan^{1*}, Abubakar Mansur Ibrahim², Umar Lawan Musa², Aminu Ahmed², Sunusi Yahaya²

^{1*} 114 Gwangwazo

² Department of chemistry Aliko dangote university of science and technology wudil

Received: 2024-10-11

Accepted: 2024-12-17

Published: 2024-12-18

ABSTRACT

Metal complexes of Co(II), Ni(II) and Zn(II) complexes of Schiff base derived from 2-aminothiophenol and 2-methoxyphenylacetaldehyde have been synthesized and characterized by conductivity measurement, magnetic measurement and spectroscopic analysis. Infrared spectra of the Schiff base revealed azomethine peak at 1640 cm⁻¹. This band was shifted to higher or lower wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M-N), also a new peak in the range of 717 – 786 cm⁻¹, the participation of the SH group in chelation is ascertained from the shift of the ν (C-S) from 730 cm⁻¹ and 758 cm⁻¹ to lower or higher wave numbers in the spectra of the complexes. Similarly a weak band of S-H, which appeared at 2620 cm⁻¹ in the case of ligand has been disappeared in the spectrum of all complexes. New bands at 780-750 cm⁻¹ in metal complexes, have been assigned to ν (M-N) mode. New bands at 660-700 cm⁻¹ in L metal complexes, have been assigned to ν (M-O) mode. Conductance measurement (1.64 – 30.50 Ohm⁻¹ cm² mol⁻¹) suggested the non-electrolytic nature of all the complexes. Magnetic susceptibility analysis of the complexes gave results in the range of 1.94 – 5.32 B.M. suggesting octahedral geometry for all the complexes. The metal ligand reacting ratio was confirmed by Jobs method of continuous variation. From the Job's plot the number of coordinated ligand was determined which indicate a 1:2 metal ligand ratio for the metal complexes. The Schiff base and its metal chelates were screened for antimicrobial activity against six pathogenic microbes (Staphylococcus aureus, Escherichia coli, Candida albican, and Mucor indicus), the Schiff base shows moderate activity, while the complexes show higher antimicrobial activity against the tested microbes.

Keywords: Amino thiophenol, methoxy, phenylacetaldehyde, tridentate

Introduction

Schiff bases, named after its inventor Hugo Schiff (Schiff 1864), are organic compounds containing azomethine group ($-C=N$). They have a general formula $R_1R_2C=NR_3$, where R_1 and R_3 are organic groups (alkyl or aryl) and R_2 may be an alkyl/aryl group or hydrogen. Schiff base metal complexes preface a new era with multipurpose activities in the coordination chemistry and also has attracted enormous interest in the field of inorganic synthesis chemistry due to the reaction and coordination mode currently. The binding ability of Schiff base with various metal ion offers stable metal complexes with unique character and versatile application [1,2,3]. Medicinal inorganic chemistry is a rapidly developing field with enormous potential applications and offers new possibilities to the pharmaceutical industry. Metal-based complexes seem to be the one of the best therapeutic approaches to treat and diagnose the diseases. The use of transition metal complexes as therapeutic compounds has become more and more pronounced. Development of transition metal complexes as drugs is not an easy task; considerable effort is required to get a compound of interest. Beside all these limitations and side effects, transition metal complexes are still the most widely used chemotherapeutic agents. Copper exhibits considerable biochemical action either as an essential trace metal or as a constituent of various exogenously administered compounds in humans [4,5].

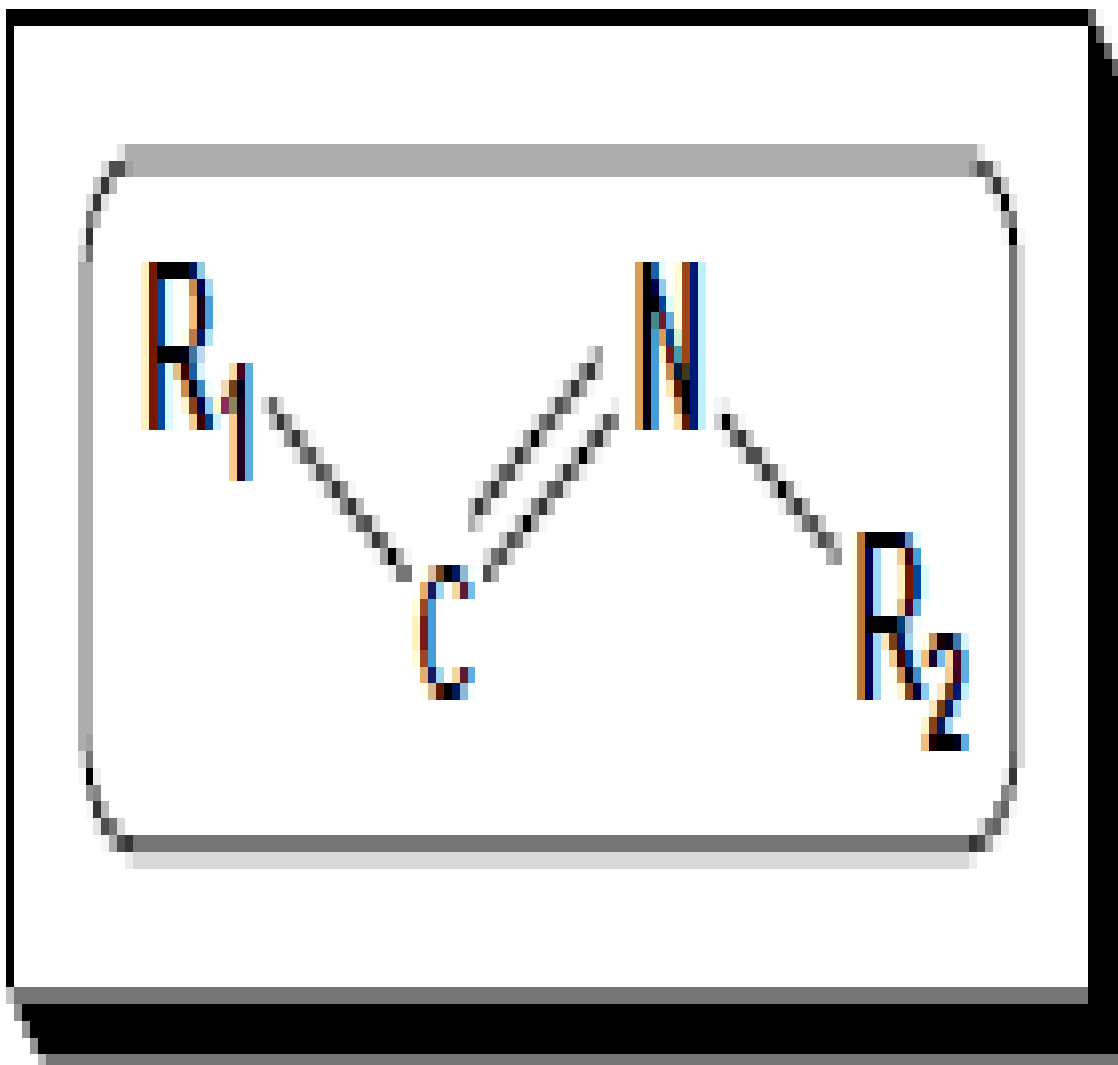
One of the most fascinating areas in coordination chemistry is the interaction of metal ions with biological molecules. All metals will form coordination compounds. The structure of metal complexes consists of a central metal atom, bonded to a surrounding array of molecules or anions [6,7].

In nature the role of coordination compounds is very important. Most of the metal ions are essential to maintain human homeostasis and also play crucial roles in many biological

processes by acting as cofactors in the proteins function thereby resulting in the stabilization, regulation and completion courses of cellular functions [8].

Chlorophyll, hemoglobin and vitamin B12 are some examples for such metal complexes. Inorganic medicinal chemistry and metal-based complexes seem to be one of the best therapeutic approaches to treat and diagnose the diseases [9,10]

On reviewing the literature, it is confirmed that metal complex exhibits greater biological property than that of free organic compounds [11, 12]. reviewed historical development and amazing broad uses of metals, and the importance of their complexes in the medical area [13].



Materials and Methods

Chemicals, Reagents and Apparatus

All the chemicals and reagents used in this research were of analytical grade and were used without further purification. All glass wares used were washed with detergent, rinsed with distilled water and dried in an oven at 110°C before use. All weighing was carried out on an electric Metler balance model H3OAR.

Preparation of the Schiff base

The Schiff base formed from 2-aminothiophenol and 2-methoxyphenylacetaldehyde was prepared by adding 20cm³ ethanolic solution of 2-aminothiophenol (1.00g, 0.00751mol) to the same volume of ethanolic solution of 2-methoxyphenylacetaldehyde (1.1278g, 0.00751mol). The mixture was magnetically stirred at 70°C for 4hrs. The reaction mixture was concentrated, cooled to room temperature to afford a crude product which was allowed to stand for 72hr. The dark solid product obtained was filtered, re-crystallized with ethanol, and washed with distilled water and dried in desiccators over CaCl₂ for 24hours [14, 15].

Preparation of Schiff base Metal Complexes

The metal complexes were prepared by adding 20cm³ of ethanolic solution of MCl₂.nH₂O (where M = Co, Cu, Mn, Fe, Ni or Zn) with ethanolic solutions of the prepared Schiff base in the ratio of (1:2). The resulting mixture was magnetically stirred at 70°C for 3hours. On cooling to room temperature, coloured solids were precipitated out. The product was filtered, re-crystallized with ethanol, and washed with distilled water and dried in a desiccator over CaCl₂ for 24hours.

Physical measurements

IR spectra of the Schiff base and its metal complexes were recorded on FTIR Carry Agilent Technologies model 630 spectrophotometer at 4000 - 650 cm⁻¹ region in KBr powder. Metal to ligand ratio was determined by using job's method of continuous variation. Jenway 4010 conductivity meter was used in conductivity measurement using DMSO as solvent.

SMP10 STUART melting point apparatus was used to obtain Melting point and decomposition temperature.

UV-visible spectrophotometric analysis was carried out using UV-visible spectrophotometer model 3310. Magnetic measurements of the complexes were performed on Gouy's balance at room temperature.

Microbial activities

The antibacterial activity of the Schiff base ligand and its metal complexes was carried out by using bacterial isolates of *Staphylococcus aureus*, and *Escherichia coli*. The suspension of each microorganism was smeared on the surface of the solidified Muller-Hinton Agar (MHA) already poured into petri dishes.

The Schiff base and the metal Complexes were separately dissolved in DMSO to obtain three distinct concentrations (250µg/disc, 125µg/disc and 62.5µg/disc) through serial dilution and placed on the surface of the culture media, incubated at 37°C for 24 hours.

Activities were determined by measuring (mm) the diameter of the zone of inhibition and compared with a standard drug (Ciprofloxacin) [16, 17].

The antifungal activity of the Schiff base ligand and that of its metal complexes were tested against two pathogenic fungi; *Candida albicans*, and *Aspergillus fumigatus*, using disc diffusion method.

Ketoconazole was used as standard fungicide and DMSO was used as a negative control The fungal suspension was smeared on the solidified Potato Dextrose Agar (PDA) already poured into petri dishes.

The Schiff base and the metal Complexes were separately dissolved in DMSO to have three different concentrations (250µg/disc, 125µg/disc and 62.5µg/disc) per well.

They were placed on the surface of the culture media and allowed to stand at room temperature for good 48 hours.

Activities were determined by measuring (mm) the diameter of the zone of inhibition and compared with the standard [18]. The sensitivity results of the biological activity of the Schiff base ligand and the metal complexes.

Results and Discussion

Table 1: Physical Properties of the Schiff base and its Metal (II) Complexes

Compounds/ Complex	Molecular weight	Colour	Percentage Yield	Melting Point	Decomposition Temperature
Ligand	257.35	Yellow	83.12	176	
[CoL ₂ Cl ₂]	645.11	Light Brown	70.24	–	259
[NiL ₂ Cl ₂]	644.91	Light Brown	68.90	–	289
[ZnL ₂ Cl ₂]	651.21	Light Brown	72.87	–	229

L = Ligand, C₁₅H₁₅NOS Mol. weight = 257.35

The Schiff base and its metal (II) complexes were prepared in good yield, the physical properties of the synthesized Schiff base and its metal complexes were analyzed and presented in Table 1.

The percentage yield of the Schiff base is 83.12% a yellow crystal, while the cobalt (II), nickel (II), and zinc (II) complexes were obtained as light brown crystal powder with a good yield of 70.24%, 68.90%, 72.87% for the cobalt, nickel and zinc complexes respectively. The decomposition temperatures of the metal complexes range from 229°C-291°C showing that the decomposition temperatures of the metal (II) complexes are higher than that of melting point of the ligand indicating that complexation has taken place [19,20].

Table 2: Solubility Test of the Schiff base and its Metal (II) Complexes

Ligand/Complexes	Distilled water	Ethanol	Methanol	Acetone	Pet. ether	DMF	DMSO
Ligand	IS	S	S	IS	IS	S	S
[CoL ₂]	IS	S	S	IS	IS	S	S
[NiL ₂]	IS	S	SS	IS	IS	S	S
[ZnL ₂]	IS	S	S	IS	IS	S	S
L=Ligand C ₁₅ H ₁₅ NOS Mol. weight=257.35 DMF=Dimethylformamide,							
DMSO=Dimethylsulfoxide, S= Soluble SS= Slightly Soluble IS= Insoluble							

Table 2 above shows the solubility of the Schiff base and its complexes. Both the Schiff base ligand and their complexes were found to be soluble in ethanol, methanol, DMF and DMSO, but insoluble in water petroleum ether, and acetone, indicating that these compounds have low polarity.

The differences in the solubility of the ligand and their corresponding complexes further proved that the synthesized complexes are different from their parental ligand

Table 3: Percentage of Water of Crystallization

Complexes	initial weight (g)	weight loss (g)	% water of crystallization	Number of water of crystallization
Co^{2+}	0.2	0.0175	8.75	4
Ni^{2+}	0.2	0.0145	7.25	3
Zn^{2+}	0.2	0.0098	4.90	2

The above table 3 shows the percentage of water of crystallization in the complexes.

All the complexes were found to be hydrated due to the presence of broad peak around 3238-3029 cm^{-1} in the Schiff base and their corresponding complexes indicate the presence of water of hydration to the structure of the compounds.

Table 4: Percentage Compositions and Empirical Formula of the Complexes

Complex	% of Metal	% of Chlorine	% of ligand	% of Water	M:L ratio	Empirical Formulae
Co ²⁺	8.2	9.9	71.8	7.5	1:2	[CoL ₂ CL ₂].4H ₂ O
Ni ²⁺	8.4	10.0	73.6	7.7	1:2	[NiL ₂ CL ₂].3H ₂ O
Zn ²⁺	9.5	10.3	75.0	7.9	1:2	[ZnL ₂ CL ₂].2H ₂ O

above table 4 shows the percentage of water of crystallization in the complexes. All the complexes were found to be hydrated where Co(II) complex was found to be tetrahydrate, Ni(II) complex was found to be trihydrate and the Zn(II) complex dihydrate.

The metal ligand reacting ratio was confirmed by Jobs method of continuous variation. From the Job's plot the number of coordinated ligand was determined which indicate a 1:2 metal ligand ratio for the metal complexes.

Table 5: Conductivity Measurements

Complexes	Electrical Conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$) $\times 10^{-6}$	Molar Conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
[CoL ₂]	32.71	10.02
[NiL ₂]	16.34	6.40
[ZnL ₂]	10.55	5.51

The molar conductance of each of the metal (II) complex was measured in dimethylsulfoxide (DMSO). The values obtained were in the range of 5.51-12.08 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Which are relatively low, indicating the non-electrolytic nature of the metal complexes? [21, 22]. The molar conductance ranges for non-electrolyte metal complexes in DMSO is 1-50 $\text{ohms}^{-1} \text{cm}^2 \text{mol}^{-1}$ [23].

Table 6: Magnetic Susceptibility

Complex	X _g ($\text{ergG}^{-2} \text{g}^{-1}$)	X _m ($\text{ergG}^{-2} \text{mol}^{-1}$)	μ_{eff} (B.M)
[CoL ₂]	$5.11 * 10^{-11}$	$4.49 * 10^{-9}$	3.97
[NiL ₂]	$1.67 * 10^{-11}$	$1.75 * 10^{-9}$	3.04
[ZnL ₂]	$-1.71 * 10^{-11}$	$-2.14 * 10^{-9}$	0

Table 6 shows the magnetic susceptibility measurement of the complexes. The effective magnetic moments of the complexes, as determined from the magnetic susceptibility, were 3.97BM for Co(II), 3.04BM for Ni(II), and 0BM for Zn(II). Based on these values we propose octahedral geometry to all the complexes.

Table 7: FTIR Spectrum

	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{OME})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{M})$	$\nu(\text{O}-\text{M})$	$\nu(\text{C}-\text{S})$
LIGAND	1640	1599	1279	1348	-	-	
[CoL ₂]	1629	1491	1279	1343	765	672	739
[NiL ₂]	1600	1493	1287	1348	736	680	740
[ZnL ₂]	1564	1510	1279	1349	770	675	742

Range 650-4000 cm^{-1} help to indicate regions of absorption vibrations. The main stretching modes are for $\nu\text{S-H}$, $\nu\text{C}=\text{N}$, $\nu\text{C}=\text{C}$, $\nu\text{C}-\text{O}$, $\nu\text{C}-\text{N}$, $\nu\text{C}-\text{S}$, $\nu\text{M}-\text{N}$, $\nu\text{M}-\text{O}$ and $\nu\text{M}-\text{S}$. The IR data of the spectra of Schiff base ligand (L) and their complexes are presented in Table below. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The position and/or the intensities of these peaks are expected to change upon chelation. Upon comparison, it was determined that the $\nu(\text{C}=\text{N})$ stretching vibration is found in the free ligands at 1640 cm^{-1} for the L ligands. This band was shifted to higher or lower wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M-N). The bands appearing between

1475 and 1600 cm^{-1} have been assigned to aromatic $\nu\text{C}=\text{C}$. The shifted band in many cases is coincident with the $\text{C}=\text{C}$ band, which then shows greater intensity or broadening.

The $\nu\text{C}=\text{N}$ modes are often mixed with higher frequency $\nu\text{C}=\text{C}$ (near 1600 cm^{-1}) and are seen as a strong band. The bands appearing at 1315-1400 cm^{-1} (specially the highest frequency ones near 1400 cm^{-1}) have been assigned to $\nu\text{C}-\text{N}$ mode. However, the participation of the SH group in chelation is ascertained from the shift of the $\nu(\text{C}-\text{S})$ from 730 cm^{-1} and 758 cm^{-1} to lower or higher wave numbers in the spectra of the complexes. Similarly a weak band of S-H, which appeared at 2620 cm^{-1} in the case of ligand has been disappeared in the spectrum of all complexes. New bands at 780-750 cm^{-1} in L metal complexes, have been assigned to $\nu(\text{M}-\text{N})$ mode. New bands at 660-700 cm^{-1} in L metal complexes, have been assigned to $\nu(\text{M}-\text{O})$ mode.

Micribial Studies

The in vitro antibacterial and antifungal screening results are given in Table 8 and 9 respectively. DMSO was used as a negative control and Ciprofloxacin was used as positive control for antibacterial and ketoconazole for antifungal activities. The results show that most of the complexes are more active than the Schiff base but much lower than the standard drugs used. In some cases, most especially in the antifungal screening, the Schiff base and the complexes have similar activities which are much lower than the ketoconazole standard. In the antibacterial, the complexes activity was fairly similar to those of the Schiff base, suggesting that the chelation has not have much impact on the isolates unlike in the bacterial isolates.

The improved activity of the metal complexes when compared with the free Schiff base in the antibacterial test may be linked to the influence of the metal ion in the cell membrane of the isolates. In addition, chelation may also play a role as it provides both the polar and non-polar properties together, needed for permeation to both the cells and the tissues.

Also, lipophilicity is modified by coordination, which may make the complexes more active than the free Schiff base [24] Though, in some cases complexation improves activity, it was found to be lower than the activity of the standards (positive control) for both the antibacterial and antifungal screening [25].

Table 8: Antifungal sensitivity test of the Schiff base and its metal (ii) complexes

Complexes	Concentration (ug/ml)/ Zone of inhibition (mm)					
	<i>Staphylococcus Aureus</i>			<i>Escherichia Coli</i>		
	250	125	62.5	250	125	62.5
Ligand	18	14	11	19	13	10
[CoL ₂]	24	18	15	15	14	11
[NiL ₂]	23	19	12	23	20	15
[ZnL ₂]	25	21	15	21	17	14
Standard	32			27		

Standard = Ciprofloxacin

Table 9: Antifungal sensitivity test of the Schiff base and its metal (ii) complexes

Complexes	Concentration (ug/ml)/ Zone of inhibition (mm)					
	<i>Candida albican</i>			<i>Mucur specie</i>		
	250	125	62.5	250	125	62.5
Ligand	18	16	17	18	16	13
[CoL ₂]	22	19	14	19	15	12
[NiL ₂]	23	18	10	13	12	-
[ZnL ₂]	17	13	10	20	18	15
Standard	38			36		

Standard = Ketoconazole

Conclusion

The Schiff base and its metal complexes of Co(II), Ni(II), and Zn(II) have been synthesized and studied by various analytical techniques. Job's method of Continuous variation shows that the metal-ligand ratio in all the complexes is 1:2. All the complexes are non-electrolytes in DMSO solvent. The decomposition temperature of the metal (II) complexes indicated that complexation has taken places. Based on magnetic susceptibility data, Co(II) and Ni(II) Schiff base complexes are paramagnetic while Zn(II) complex is diamagnetic.

Based on the spectral studies, conductance data and magnetic susceptibility data, the synthesized ligand and its complexes are neutral tridentate, coordinating through the Oxygen of the methoxy group, Sulphur of thiol and Nitrogen of the azomethine group. The antimicrobial activity results indicate that all complexes have been found to be more effective than its ligand as the process of chelation dominantly affects the overall biological behavior of the compounds. Based on the analytical and spectral studies, we propose octahedral geometry to all the complexes.

Reference

- [1] U. Reece, L. Urry, *Campbell Biology* Pearson Benjamin Cummings New York., 65 83 (2011)
- [2] E. Malle, *Br. J. Pharm.*, 152(6) 838-854 (2007).
- [3] M. R. Chedekel, D. E. Sharp, G. A. Jeffery, *Synth. Commun.*, 10 167-173 (1980).
- [4] A. Kumar, R. Kumar, *Int. Res. J. Pharm.*, 2 11-12 (2011).
- [5] H. Keypour, M. Rezaeivala, L. Valencia, P. Perez Lourido, H. Razakhavasi, *Polyhedron*, 28 3755-3756 (2009).
- [6] K. Patick, K. E. Potts, *Clin. Microbiol. Rev.*, 11 614-627 (1998).

- [7] M. M. T. Khan, S. B. Hulligudi, S. Shukla, Z. A. Shaikh, *J. Mol. Catal.*, 57 301-305 (1990).
- [8] S. Bharti, M. Choudhary, B. Mohan, S. P. Rawat, *J. Mol. Struct.*, 1164 137-154 (2018).
- [9] B. Shafaatian, S. S. Mousavi, S. Afshari, *J. Mol. Struct.*, 1123 191-198 (2016).
- [10] H. Kargar, M. Ashfaq, M. N. Tahir, *J. Mol. Struct.*, 1261 132905 (2022).
- [11] R. S. Yamgar, Y. Nivid, S. Nalawade, M. Mandewale, R. G. Atram, S. S. Sawant, *Bioinorg Chem Appl.*, 276598 (2014).
- [12] M. Kumar, S. Chauhan, S. Garg, *J. Indian Chem. Soc.*, 100(2) 100797 (2023).
- [13] A. Salomanravi, R. Asha, V. Veeraputhiran, P. Muthuselvan, *J. Adv. Sci. Res.*, 13(01) 167-176 (2022).
- [14] M. N. Uddin, D. A. Chowdhury, M. M. Rony, M. E. Halim, *Modern Chem.*, 2(2) 6-13 (2014).
- [15] M. M. Hossain, M. A. Bashar, M. N. Khan, P. K. Roy, M. A. Mannan, M. S. Ali, M. A. Farooque, *Am. J. Appl. Chem.*, 6(4) 147-155 (2018).
- [16] J. A. Shampa, M. R. Islam, M. S. Hossain, G. T. Rahman, C. M. Zakaria, M. Kudrat-E-Zahan, *Am. J. Heterocycl. Chem.*, 3(4) 37-41 (2017).
- [17] Z. H. Chohan, M. F. Jaffery, C. T. Supuran, *Metal Based Drugs*, 8(2) 95-101 (2001).
- [18] N. K. Chaudhary, P. Mishra, *J. Chem.*, 12 pages (2015).
- [19] M. Montazerzohori, M. Sedighipoor, S. Joohari, *Int. J. Electrochem. Sci.*, 7 77-88 (2012).
- [20] D. A. Chowdhury, M. N. Uddin, F. Hoque, *Chiang Mai J. Sci.*, 37(3) 443-450 (2010).
- [21] D. A. Chowdhury, M. N. Uddin, M. A. H. Sarker, *Chiang Mai J. Sci.*, 35(3) 483-494 (2008).
- [22] D. A. Chowdhury, M. N. Uddin, G. K. Chowdhury, *The Chitt. Uni. J. of Sci.*, 30(1) 85-88 (2006).
- [23] M. N. Uddin, D. A. Chowdhury, K. Hossain, *J. Chinese Chem. Soc.*, 59(12) 1520-1527 (2012).

[24]C. Spinu, M. Pleniceanu, C. Tigae, *Turk. J. Chem.*, 32 487–493 (2008).

[25]C. E. Benjamin, A. O. Sulaiman, A. Oluwatoba, A. Oladipo, E. Oluwatomisin, *J. Appl. Sci.*, 8(8) (2018).

HOW TO CITE THIS ARTICLE

Ishaq Yahaya Lawan; Abubakar Mansur Ibrahim; Umar Lawan Musa; Aminu Ahmed; Sunusi Yahaya. "**Metal complexes of Co(II), Ni(II) and Zn(II) complexes of Schiff base derived from 2-aminothiophenol and 2-methoxyphenylacetaldehyde, synthesized, characterized and their microbial activity**", *International Journal of New Chemistry.*, 2025; 12(4), 656-671. doi: 10.22034/ijnc.2023.2007951.1350