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Synthesis, Characterization and Antimicrobial Studies of Schiff Base Derived from the Reaction of 2-Thiophenecarboxaldehyde and Ethylenediamine and its Metal (II) Complexes

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ABSTRACT

Schiff base was derived by condensation of 2-thiophenecarboxaldehyde and ethylenediamine. Its Mn(II), Fe(II) and Co(II) complexes have been prepared and characterized on the basis of melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility, elemental analysis, infrared spectroscopic analysis and UV-visible spectrophotometry. The Schiff base and complexes were found to be soluble in DMSO, DMF and some organic solvents thus, they are non-ionic compounds. The Decomposition temperatures of the complexes were found to be within the range of 173-246°C, showing the stability of the complexes. All the complexes have low molar conductance values (8.66-25.29 Ω^{-1} cm^2 mol^{-1}) indicating their non- electrolytic nature. Magnetic moment values of the complexes were found to be within the range of 3.847BM - 5.12BM which indicated that they are paramagnetic. Infrared spectra of the Schiff base indicated the azomethine peak at 1629cm^{-1} which shifted to the lower frequencies (1603-1562cm^{-1}) in the spectra of the complexes. Both analytical and spectroscopic data showed that the complexes were formed and the coordination sites were through the nitrogen of the azomethine (-HC=N-) group and the sulfur atom of the thiophene ring. 1:1 metal-ligand ratio was suggested The Schiff base and its complexes have been screened for their *in vitro* antimicrobial activity against three pathogenic bacteria (*Staphylococcus aureus, Streptococcus pneumonia and Escherichia coli)* and two pathogenic fungi *(Aspergillus niger* and *Aspergillus flavus).* The Schiff base shows moderate inhibition zone (06 - 14) whereas some of the metal chelates show slightly higher inhibition zone (06 - 17) mm against the bacteria and fungi but lower than that of the control drugs used (18-30) mm.

Keywords: 2-thiophenecarboxaldehyde, antimicrobial, ethylenediamine, Schiff base

INTRODUCTION

Schiff bases are synthesized from the condensation of primary amines with carbonyl groups (Shrivastava and Shrivastava, 2016). Ever since the German Chemist, Hugo Schiff used amines in 1864 to make several “metallo-imines”, numbers of variants of the condensation products of amines and aldehydes or ketones such as RCH=NR’ where R and R’ are alkyl and/or aryl substituents, are popularized. They are also known as Schiff bases, anils, imines or azomethines (Mangamamba *et al*., 2014). Schiff bases are capable of forming coordinate bonds with many metal ions via azomethine group, and so they have been used for the synthesis of metal complexes due to their easy formation and strong metal binding ability, they are generally bi-, tri- or tetra- dentate ligands capable of forming very stable complexes with transition metals (Arulmurugan *et al*., 2010). In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds. Their corresponding metal complexes have expanded enormously and include a vast area of organometallic compounds and various aspects of bioinorganic chemistry (Sha *et al*., 2017) Schiff bases are one of the important compounds with wide range of biological activities and industrial applications (Zemede *et al*., 2015). Complexes of Metal (II) ion containing Schiff bases possess remarkable properties as catalysts in various biological systems (Zoubi, 2013; Abu-dief and Mohammed, 2015; Maity, 2019), polymers (Mighani, 2020; Sanchez *et al* 2014) dyes (Abuamer *et al*., 2014), antibacterial and antifungal activities (Jameel *et al*., 2014), antiviral activities (Kajal *et al*., 2013) anti-inflammatory (Jesmin *et al*.,2014), pesticidal, antitumor and cytotoxic activities (Katwal *et al*., 2013; Sarkar and Dey 2005) . They also possess wide applications in analytical chemistry, agrochemical and pharmaceutical fields (Bitu *et al*., 2019).The advances in inorganic chemistry provide better opportunities to use the metal complexes as therapeutic agents. They contributed a lot in the development of metal based drugs with promising pharmacological application and may offer unique therapeutic opportunities, for instance, the clinical application of chemotherapeutic agents for cancer treatment, such as cisplatin (Rafique *et al*., 2010). Complexes of Mn(II) and Co(II), Ni(II) Co(II) and Zn(II) with N-(2-Chloro-phenyl)-N'-thiophen-2-ylmethylene-hydrazine were synthesized by condensation reaction of (2 thiophenecarboxaldehyde and 2-chlorophenyl hydrazine) and characterized by Elemental analysis, magnetic and spectroscopic measurements, infrared spectroscopy, X-ray powder diffraction and scanning electron microscopy. Infrared spectra of the complexes agreed with the coordination to the central metal atom through the nitrogen of the 2-chlorophenyl hydrazine and the sulfur atom of the thiophene ring. The Schiff base and its metal chelates were screened for their *in vitro* antibacterial activity against *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus flavus* and *Candida albicans.* The metal chelates were shown to possess more antibacterial activity than the free Schiff-base (Refat *et al*, 2014). Complexes of Mn(II), Cu(II) and Ni(II) with Schiff base derived from condensation of propionaldehyde with ethylenediamine were synthesized in alcoholic medium. The complexes were characterized on the basis of melting point, conductivity, solubility, FT-IR and UV/Visible spectral studies. The *in-vitro* antibacterial activities of the complexes were tested against different strains of bacteria *Staphylococcus aureus, Streptococcus pyogenes, Escherichia coli, and Salmonella typhi* and fungus *Candida albicans* (Wakil *et al*, 2017).

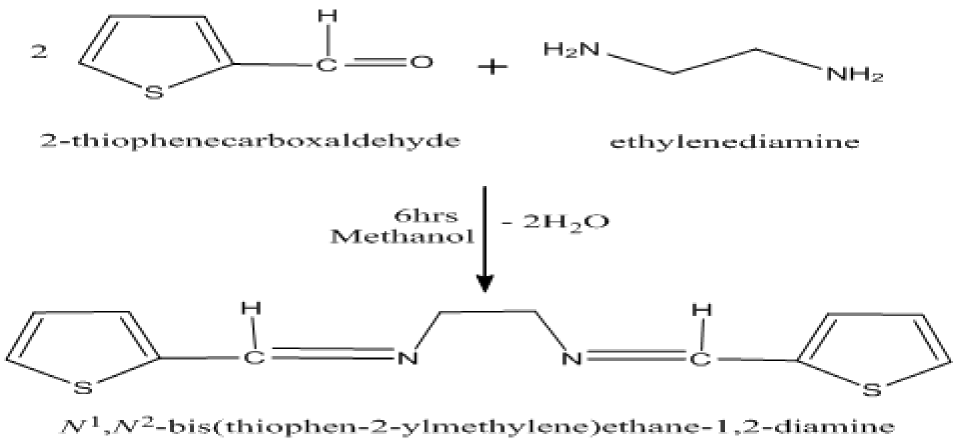
MATERIALS AND METHODS

Chemicals, Reagents and Apparatus

All the chemicals and reagents used in this researchwere 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.

Synthesis of the Schiff base Ligand

Ethylenediamine (15 mmol) in 30ml of methanol was added drop wise to a solution of 2-thiophenecarboxaldehyde (30 mmol) in 30 mL of methanol with continuous stirring. The solution was refluxed for 6 hours and then cooled in ice for 1hr. The brown product formed after cooling (Scheme 1) was then filtered off, washed with ethanol and dried in a desiccator containing anhydrous phosphorous pentaoxide (Uddin *et al*., 2014).



Scheme 1: Synthesis of Schiff base

Synthesis of the metal(II) Schiff Base Complexes

The metal complexes of the Schiff base were prepared by the addition of a hot solution (60◦C) of the appropriate metal chloride (30 mmol) in an ethanol-water mixture (1:1, 25 mL) to the hot solution (60◦C) of the Schiff base (30 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for 4 hours where upon the complexes precipitated. They were collected by filtration, washed with 1:1 ethanol-water mixture and diethyl ether, dried in a desiccator containing phosphorous pentaoxide (Uddin *et al*., 2014).

Physical measurements

IR spectra of the Schiff base and its metal complexes were recorded on FTIR Carry Agilent Technologies model 630 spectrophotometer at 4000 - 400 cm^{-1} region in KBr powder. C, H and N were estimated by using elemental analyzer Perkin-Elmer model 240c. Jenway 4010 conductivity meter was used in conductivity measurement using DMSO as solvent. SMP10 STUART melting point apparatus was used to obtained 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.

Antibacterial and Antifungal Test

The *in vitro* antibacterial test of the Schiff base and its metal (II) complexes were studied using bacterial isolates: *Staphylococcus aureus, Streptococcus pneumonia, and Escherichia coli* by agar well diffusion method using nutrient agar as medium (Jain and Mishra, 2010). The suspension of each microorganism was smeared on the surface of solidified Muller-Hinton Agar (MHA) already poured into Petri dishes. The antibacterial assay was evaluated using different concentrations of the ligand and the metal (II) complexes. The stock solution was prepared by dissolving 0.01g of the Schiff base and each of the metal(II) complexes separately in 1ml of Dimethylsulphoxide (DMSO) which serves as diluent and these yielded 100mg/ml. From the stock solution, four different concentrations (4000 µg /ml, 2000 µg /ml, 1000 µg /ml and 500 µg /ml) were prepared through serial dilution and placed on the nutrient agar before incubation at 37^0C for 24 hours (Bukar *et al*., 2009). During this period, the test solution diffused and the growth of the inoculated microorganism was affected. The inhibition zone was measured in (mm), at which the concentration were taken and recorded. Similar procedure was applied in antifungal Evaluation by using *Aspergillus flavus* and *Aspergillus niger* fungal isolates at room temperature for 72 hrs.

RESULTS AND DISCUSSION

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

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 was 64 % while that of the complexes were 58, 82 and 65%. The Schiff base was yellow while the Mn(II) , Fe(II) and Co(II)complexes were found to be brown, green and dark brown respectively. It was found that the melting point of the Schiff base was 109 ^{O}C and the decomposition temperature of the metal (II) complexes were 232, 246 and 173^OC, this indicated that they are thermally stable complexes.

Molar conductance of the metal complexes were 8.66, 10.32and $25.29\Omega^{-1}cm^2mol^{-1}$ for Mn(II), Fe(II) and Co(II) complexes. These low values of their molar conductance suggest their non-electrolytic nature (Spinu, 2008). The effective magnetic moments of the complexes were also calculated. The magnetic moment of Mn(II) complex was 5.12 B.M, while that of Fe(II) complex was 4.36 and that of Co(II) was 3.84. These showed their Paramagnetism and were within the range of octahedral geometry values of the metal(II) complexes.

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

Compounds	Colour	%	M.P.	D. T.	μ_B	ML
L	Yellow	64	109	-	-	-
[$MnLCl_2$]	Brown	58	-	232	5.12	8.66
[$FeLCl_2$]	Green	82	-	246	4.36	10.32
$CoLCl_2$]	Dark brown	65	-	173	3.84	25.29

Keys: L = $C_{12}H_{12}N_2S_2$, M.P = Melting Point, D. T. = Decomposition temperature and M.L= Molar conductivity

Solubility Test

Water and some common organic solvents were used to determine the solubility of the Schiff base and its metal (II) complexes. From the result of solubility test presented in Table 2, it can be observed that, the Schiff base and its metal complexes were soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF), slightly soluble in ethanol and insoluble in diethyl ether, n-hexane and water. Therefore the compounds were suggested to be nonionic in nature.

Table 2: Solubility test of the Schiff base and its metal (II) complexes

Solvents	L	[$MnLCl_2$]	[$FeLCl_2$]	[$CoLCl_2$]
Acetone	S	IS	IS	IS
Chloroform	S	SS	IS	IS
Diethylether	IS	IS	IS	IS
Ethanol	SS	SS	SS	SS
Hexane	IS	IS	IS	IS
Methanol	SS	SS	SS	SS
DMF	S	S	S	S
DMSO	S	S	S	S
Water	IS	IS	IS	IS

Keys: L = $C_{12}H_{12}N_2S_2$, DMF =Dimethylformamide, DMSO = Dimethylsulphoxide S = Soluble, SS = Slightly Soluble, and IS = Insoluble

Elemental Analysis

The elemental analysis of the Schiff base and its metal(II) complexes were determined and presented in Table 3, in which percentages of carbon, hydrogen and nitrogen in the compounds were set to be found. The values obtained showed a reasonable agreement with the calculated values for the corresponding elements in all the complexes and were suggested to be 1:1 metal: ligand stoichiometry for the mononuclear complexes. The data for Schiff base suggested the formation of $C_{12}H_{12}N_2S_2$while that of complexes suggested the formation of [$MnLCl_2$], [$FeLCl_2$] and [$CoLCl_2$].

Table 3: Elemental Analysis Data of the Schiff base and its Metal (II) Complexes

COMPOUNDS	% C	% H	% N
L	57.72 (58.02)	3.92 (4.87)	10.64 (11.28)
[$MnLCl_2$]	39.48 (38.50)	3.48 (3.23)	9.01 (7.41)
[$FeLCl_2$]	37.44 (38.41)	4.39 (3.23)	7.02 (7.47)
$CoLCl_2$]	38.60 (38.10)	3.00 (3.19)	7.11 (7.41)

Key: L = $C_{12}H_{12}N_2S_2$

FTIR Analysis

The FTIR results of the Schiff base and metal complexes together with their spectral data are presented in Table 4.The band at 1629 cm^{-1} in the free Schiff base is assigned to the *v*(C=N) stretching vibration. This band shifted towards lower frequencies of 1588 and 1562 and 1603 cm^{-1} in the complexes, and this suggested the participation of the nitrogen atom of the azomethine in coordination. The Schiff base coordination with the metals is further evidenced by the appearance of weak low frequency non ligand bands at 641, 504 and 592 cm^{-1} due to *v*(M-N) stretching vibration, and at 444, 430 and 448 cm^{-1} due to *v*(M-S) stretching vibration. Similar result was reported by Refat (2014).

Table 4: Infrared spectral data of the Schiff base and its metal (II) complexes

Compound	*v*C=N (cm^{-1})	*v*M-N (cm^{-1})	*v*M-S (cm^{-1})
L	1629	-	-
[$MnLCl_2$]	1588	641	444
[$FeLCl_2$]	1562	504	430
[$CoLCl_2$]	1603	592	448

Key:L = $C_{12}H_{12}N_2S_2$

The data for electronic spectra of the Schiff base, and its complexes are given in Table 5. Two essential absorption bands were observed at 204nm and 306nm in the spectra of the Schiff base which were assigned to the transitions n→ π*, π → π*, respectively These transitions were existed also in the spectra of the complexes, but they shifted to different intensities n→ π*(220, 244, 222) and π → π* (300, 301 and 292) for Mn(II), Fe(II) and Co(II) complexes respectively, confirming the coordination of the ligand to the metal ions.

Table 5: Absorption Spectral data (nm) of the Schiff base and Metal (II) Complexes

Complex	***π-π****	**n-*π****
Schiff Base	204	306
[$MnLCl_2$]	220	300
[$FeLCl_2$]	244	301
[$CoLCl_2$]	222	292

Key: L = $C_{12}H_{12}N_2S_2$

Antimicrobial and antifungal Activity

Tables 6 and 7 show the result of antimicrobial activity of the Schiff base and its metal complexes. The Schiff base and its metal (II) complexes were screened for their antibacterial activities against the selected bacteria isolates (*Staphylococcus aureus, Streptococcus Pneumoniae and Escherichia coli)* and some selected fungal isolates (*Aspergillus flavus,* and *Asphergillus niger).* The diameter of zone of inhibition (mm) was measured for each treatment (Table 6 and 7). The results were compared with those of the standard drug ciprofloxacin for antibacteria and ketoconazole for antifungi. The Schiff base and the complexes exhibited varying degrees of inhibitory effect on the growth of the tested microbial species. The activity of the Schiff base complexes became more active when coordinated with the metal ions. The biological activities of the complexes follow the order. Antibacterial effect: Co(II) > Mn(II) > Fe(II) and Antifungal effect: Fe(II) = Mn(II) > Co(II).

Table 6: Antibacterial activity on the Schiff base and its metal (II) complexes

COMPOUNDS	***Staphylococcus Aureus***				***Streptococcus Pneumoniae***				***Escherichia Coli***			
	CONCENTRATIONS µg/ml				CONCENTRATIONS µg/ml				CONCENTRATIONS µg/ml			
	4000	2000	1000	500	4000	2000	1000	500	4000	2000	1000	500
LIGAND	14	11	9	6	12	8	8	7	13	12	9	8
$[MnLCl_2]$	16	14	11	9	13	9	9	8	6	6	6	6
$[FeLCl_2]$	16	12	10	9	12	9	7	8	6	6	6	6
$[CoLCl_2]$	17	15	12	10	14	12	9	9	16	14	10	8
CIPROFLOXACIN	25				30				27			

Key:L = $C_{12}H_{12}N_2S_2$

Table 7: Antifungal activity on the Schiff base and its metal (II) complexes

COMPOUNDS	***Aspergillus niger***				***Aspergillus flavus***			
	CONCENTRATIONS µg/ml				CONCENTRATIONS µg/ml			
	4000	2000	1000	500	4000	2000	1000	500
LIGAND	11	9	7	6	12	10	9	7
$[MnLCl_2]$	12	10	9	7	14	11	8	6
$[FeLCl_2]$	14	9	8	7	11	10	7	8
$[CoLCl_2]$	12	9	7	6	13	12	8	7
KETOCONAZOLE	22				18			

Key: L = $C_{12}H_{12}N_2S_2$

The structure of the synthesized complexes is proposed as Figure 1 according to the result obtained from spectroscopic data (FT-IR spectroscopy, and UV-visible spectroscopy) and Analytical data (elemental analysis, conductivity measurement, and magnetic susceptibility).

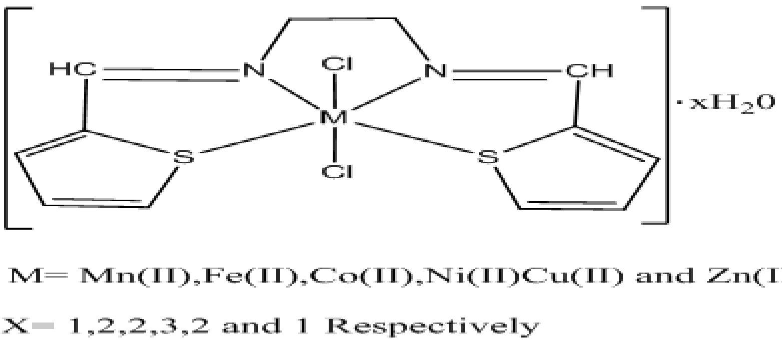


Figure 1: Proposed structure of Metal (II) Complex

CONCLUSION

The Schiff base was synthesized by condensation of ethylenediamine and 2-thiophenecarboxaldehye. The complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were also synthesized from the reaction of the Schiff base and metal (II) chlorides in ethanol/water solution. The ligand and its metal(II) complexes have been characterized by spectroscopic measurements (FT-IR, UV-visible), elemental analyses (CHN), molar conductance, magnetic susceptibility measurements, melting point, decomposition temperature and solubility test. The *in vitro* antimicrobial activity of the Schiff base and its metal (II) complexes were carried out on *Staphylococcus aureus, Streptococcus pneumonia, Escherichia coli, Aspergillus niger and Aspergillus flavus*. The results of the studies revealed that the complexes showed better activity compared to that of the Schiff base but lower than the control drugs.

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