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SYNTHESIS, CHARACTERIZATION AND ANTI-MICROBIAL ACTIVITIES OF SCHIFF BASE DERIVED FROM 2-AMINOBENZENETHIOL AND 4-NITROBENZALDEHYDE AND ITS Mn(II), Fe(II) AND Co(II) COMPLEXES

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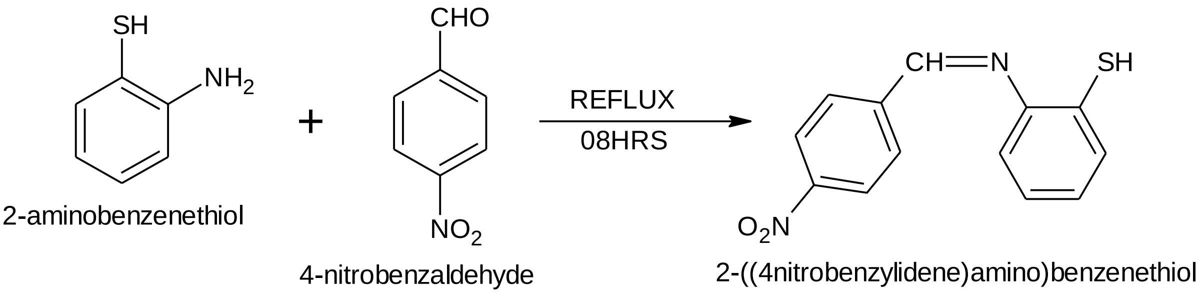
ABSTRACT
A Schiff base was prepared by the condensation of 2-aminobenzenethiol and 4-nitrobenzaldehyde. Metal (II) chlorides were refluxed with the prepared Schiff base affording the corresponding metal(II) complexes. The synthesized compounds were characterized based on T-IR, solubility test, melting point/decomposition temperature, molar conductance, magnetic susceptibility, UV-visible spectroscopy and elemental analysis. IR spectra of the Schiff base indicated the azomethine (-C=N-) peak at 1596cm^{-1}, which is shifted in the spectra of the complexes. The Schiff base melts at 160^{o}C, whereas the chelate decomposes within the range of (220^{o}C -232^{o}C). The Elemental analysis revealed the metal to ligand ratio as 1:2. Molar conductance values (11.03 $\Omega^{-1}cm^2mol^{-1}$ – 15.93 $\Omega^{-1}cm^2mol^{-1}$) showed non- electrolytic nature of the complexes, magnetic susceptibility values of the complexes were recorded at the range (4.51BM -5.85BM). The synthesized Schiff base and their respective complexes were screened for their anti-microbial activities against some selected pathogenic bacteria (*Staphylococcus aureus*, and *Escherichia coli*) and fungi (*Aspergillus niger* and *Candida albicans*), the Schiff base shows moderate activity at 6 -15mm zone of inhibition, while the metal(II) complexes show higher activity with the increased in concentration. Moreover, antifungal data revealed an appreciated activity (6 – 18) mm zone of inhibition against all fungal isolates, which is lower than the standard.

Keywords: 2-Aminobenzenethiol, 4-Nitrobenzaldehyde, Schiff base, Anti-Microbial Activity, Metal(II) Complexes

INTRODUCTION
Coordination chemistry is undoubtedly the most active area in Inorganic Chemistry, the importance of the coordination phenomenon in biological processes was realized have re, most metal containing macromolecules have been synthesized and studied to understand the role of these ligands in biological systems and they also contribute to the development of new metal-based chemotherapeutic agents. These have resulted in the emergence of an important branch of inorganic chemistry viz: bioinorganic chemistry because in several cases, the metal chelates have been found contains more antimicrobial properties than the chelating agent themselves Sakhare *et al.* 2015). Schiff bases have been considered as versatile ligands, especially in terms of their donor atoms and substituent, thereby providing the possibility for designing transition metal complexes with useful biological properties. Over the last few decades, the research field of medicinal inorganic chemistry has experienced continuous growth in the synthesis of nitrogen containing heterocyclic derivatives because of their utility in various applications. Schiff bases are compounds containing an imine or azomethine group, (-N=CH). They are condensation products of aldehydes or ketones with primary amines and were first discovered and reported by Hugo Schiff in 1864 (Hussain *et al.*, 2014).
Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, antifungal and antitumor activity (Kumar et al., 2013). A large number of Schiff bases and their complexes have been studied for their interesting and important properties examples, their ability to reversibly bind oxygen, catalytic activity in Hydrogenation of olefins and transfer of an amino- group, photo chromic properties, complexation ability towards some toxic metals (Sani and Iliyasu, 2018).

MATERIALS AND METHODS
All reagents and solvents used were of analytical grade purity and were used directly without further purification. All glasswares sed in this research work were washed thoroughly with detergent and rinsed three times with distilled water and dried in an oven at 110 ^{o}C before use. All weighing was carried out on an electric Metler balance model B154 and melting point, decomposition temperatures were determined using Stuart SMP10 melting point apparatus. IR-spectral analysis was recorded on FTIR Cary 630, Agilent Technology model. The magnetic susceptibility of the complexes was measured using Magnetic Susceptibility balance MK1. Molar conductance was determined using a Jen way 4010 conductivity meter. The elemental analysis (CHN) was carried out using PerkinElmer Series II CHNS/O Analyzer 2400, Elemental Analyzer. Bacterial and fungal isolates were obtained and identified at the Department of Microbiology, Bayero University Kano.

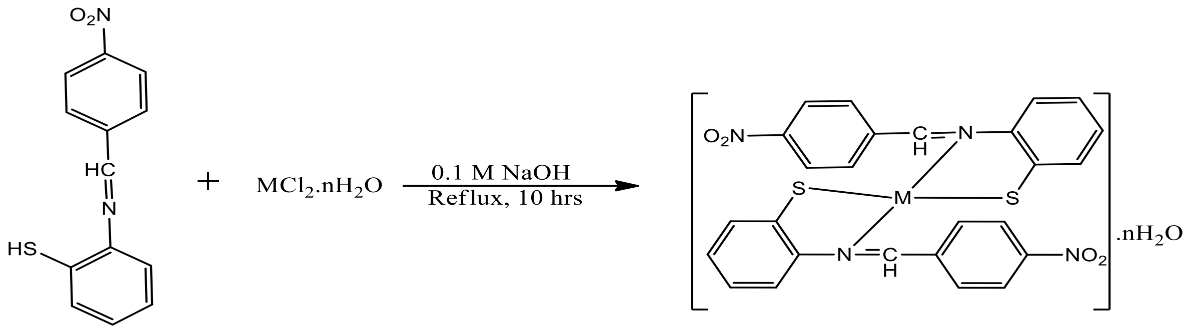
Synthesis of Schiff Base
The Schiff base was synthesized by mixing an ethanoic solution of 2-aminobenzenethiol (125.19 g, 0.01 mol) and 4-nitrobenzaldehyde (151.12, 0.01 mol). The mixture was refluxed with stirring for 8 hours. The resulting solution was concentrated to half volume and then put in a crushe ice a yellow precipitate was formed. The precipitate was collected by filtration, washed several times with cold ethanol, dried in desiccator over phosphorus pentaoxide (P_2O_5) and then in ether (Ashraf *et al.*, 2017).



Scheme 1: Synthesis of Schiff base

Synthesis of Metal(II) Complexes

The metal complexes were synthesized by mixing an ethanolic solution of the Schiff base (0.02 mol) with an ethanolic solution of the metal(II) chlorides of Mn, Co and Fe, (0.01 mol), followed by the dropwise addition of 0.1 mol NaOH solution (scheme 1). The resulting mixture was refluxed for 10 hours. On cooling, the metal complex compounds that precipitated out was filtered, washed several times with cold ethanol and finally with petroleum ether and dried over P_2O_5 in a desiccator.



Scheme 2: Synthesis of metal (II) complexes

Anti-Bacterial Activity Test

The Schiff base and complexes were screened for their activity against clinically isolated bacteria, *Staphylococcus aureus,* and *Escherichia coli*, by disc diffusion method. The suspension of each microorganism was smeared on the surface of the solidified Muller-Hinton Agar (MHA) already poured into separate Petri dishes. The Schiff base and the metal complexes were separately dissolved in DMSO to have three distinct concentrations (15 µg/disc, 30 µg/disc and 60 µg/disc) through serial dilution and placed on the surface of the culture media, incubated at 37 ºC for 24 hours. Activities were determined by measuring (mm) the diameter of the zone of inhibition and compared with a standard antibiotics drug (Ciprofloxacin), while DMSO wetted discs were used as a negative control (Yusha'u *et al.,* 2011).

Anti-Fungal Activity Test

The Schiff base and its metal complexes were tested against pathogenic fungi; *Aspergillus niger and Candida albicans* using the disc diffusion method. Ketoconazole was used as standard fungicide control and DMSO was used as a negative control, Khan *et al., (*2014). The fungal suspension was smeared on 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 (15 µg/disc, 30 µg/disc and 60 µg/disc). They were placed on the surface of the culture media and incubated at room temperature for 48 hours. Activities were determined by measuring the (mm) diameter zone of inhibition and compared with the standard.

RESULTS AND DISCUSSION

Schiff base, 2-((4-nitrobenzylidene)amino)benzenethiol, was synthesized by the condensation of 2-aminobenzenethiol and 4- nitrobenzaldehyde in ethanol. It was obtained in good yield (88 %) and purified by recrystallization in ethanol followed by washing several times with petroleum ether. The yellowish crystal was found to have a melting point of 160 ºC (Table 1). Schiff base was characterized by infrared spectroscopy, solubility, decomposition temperature, magnetic susceptibility, conductivity, elemental analysis and UV-visible. The yellowish color of the Schiff base was observed to change to other colors as shown in Table 1 upon complexation. The complexes were obtained in good yield (64-81 %), and the decomposition temperature of the metal complexes ranged (210-232) ºC, showing that the metal complexes are more stable than the Schiff base (Table 1).

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

Compounds	Colour	Melting Point (^{0}C)	Decomposition Temperature (^{0}C)	Percentage Yield (%)
Ligand	Yellow	160		86
$[MnL_2]. 2H_2O$	Light –Brown		226	68
$[FeL_2]. 2H_2O$	Golden –Brown		220	69
$[CoL_2]. 2H_2O$	Greenish –Yellow		232	76

Table 2: Solubility Test Results of Schiff base and its Metal Complexes

Compounds	H_2O	CH_3OH	C_2H_6O	n-hexane	CCl_4	Acetone	$CHCl_3$	Pet.ether	DMF	DMSO
Ligand	IS	S	IS	IS	SS	S	S	IS	S	S
$[MnL_2].2H_2O$	IS	SS	IS	IS	SS	S	S	IS	S	S
$S[FeL_2].2H_2O$	IS	SS	IS	IS	SS	S	S	IS	S	S
$[CoL_2].2H_2O$	IS	SS	IS	IS	SS	S	S	IS	S	S

Where; S= Soluble, SS= Slightly soluble, IS= Insoluble, L=$C_{13}H_9N_2SO_2$, DMSO= Dimethylsulfoxide, DMF=Dimethylformamide, CCl_4 = Carbontetrachloride, CH_3OH= Methanol, C_2H_6OH= Ethanol

The result of solubility test carried out on the Schiff base in some common solvents as presented in Table 2, showed that it is soluble in methanol, DMSO, DMF, acetone, and chloroform; insoluble in ethanol, water, petroleum ether and n-hexane; slightly soluble in carbon tetrachloride. Also, the metal complexes were soluble in DMSO, DMF, chloroform and acetone but insoluble in ethanol, water, n-hexane and petroleum ether, slightly soluble in methanol and carbon tetrachloride.

Table 3: Fourier Transform Infrared Spectroscopy (FT-IR Spectra data) of the Schiff Base and its Metal (II) Complexes

Compound	V(C=N) cm^{-1}	V(H_2O) cm^{-1}	V(M-N) cm^{-1}	V(SH) cm^{-1}	V(M-S) cm^{-1}
2-Aminobenzenethiol				2523	
L	1596				
$[MnL_2].2H_2O$	1589	3231	530		422
$[FeL_2]$ $.2H_2O$	1599	3242	567		444
$[CoL_2]$ $.2H_2O$	1588	3331	585		482

L= $C_{13}H_{10}N_2S_2O_2$

The IR spectral data of the Schiff base and the synthesized complexes are summarized in Table 3. Spectra of the Schiff base showed a strong absorption band at 1596 cm^{-1} due to *v*(C=N) stretching, indicating that condensation has taken place between CHO moiety of 4-nitrobenzaldehyde and $–NH_2$ moiety of 2-aminobenzenethiol. The IR spectra of all the compounds formed contain a band in the region of 1588-1599 cm^{-1} attributed to the azomethine (HC=N) bond which further suggested the formation of the complexes. Spectral peaks within the range of 530 -585 cm^{-1} of the chelate can be attributed to v(M-N), suggesting coordination of metal ions through the N atom of azomethine group Fasina *et al*, *(*2013). Furthermore, another additional peak in the range (422-482) cm^{-1} was attributed to M-S suggesting that the metal was coordinated to both the S and N donor atoms.

Table 4: Conductivity Measurement Data of 10^{-3} M Metal (II) Complexes in DMF

Complexes	Electrical conductance (ohm^{-1} cm^{-1}) X 10^{-6}	Molar Conductance (ohm^{-1} cm^{-2} mol^{-1})
$[MnL_2]$ $.2H_2O$	33.1	11.03
$[FeL_2]$ $.2H_2O$	47.8	15.93
$[CoL_2]$ $.2H_2O$	39.6	13.20

L= $C_{13}H_9N_2SO_2$

The molar conductance of each of the metal(II) complexes was measured in dimethylformamide (DMF) and the values obtained were in the range of 11.03 - 15.93 ohm $^1cm^2mol^{-1}$ which are relatively low, indicating the non-electronic nature of the metal(II) complexes (Table 4).

Table 5: Magnetic Susceptibility Data of Metal (II) Schiff base Complexes

Complexes	X_g(erg.g^{-2} mol^1)	X_m(erg.g^{-2} mol^1)	μ_{eff} (B.M)	Magnetic property
$[MnL_2]$ $.2H_2O$	$2.5254x10^{-5}$	$1.4368x10^{-2}$	5.85	Paramagnetic
$[FeL_2]$ $.2H_2O$	$2.3409x10^{-5}$	$1.3340x10^{-2}$	5.64	Paramagnetic
$[CoL_2]$ $.2H_2O$	$1.49x10^{-5}$	$8.53x10^{-3}$	4.51	Paramagnetic

L= $C_{13}H_9N_2SO_2$, Xg= Mass Susceptibility, Xm= Molar Susceptibility

Table 6 presents the result of magnetic susceptibility measurement of Mn(II), Fe(II), and Co(II) complexes at room temperature indicating that they are all paramagnetic (Taghreed, 2016).

Table 6: Ultraviolet-Visible Spectroscopy (UV-visible Spectral data) of Schiff base and its Metal (II) Complexes

Compound	*π-π** (nm)	n-*π** (nm)
$C_{13}H_{10}N_2S_2O_2$	212	370
$[MnL_2]$ $.2H_2O$	233	345.25
$[FeL_2]$ $.2H_2O$	235.80	361.90
$[CoL_2]$ $.2H_2O$	250.03	352.70

L= $C_{13}H_9N_2SO_2$

Table 6 shows the electronic Spectra of the Schiff base and complexes recorded in acetone. The first absorption spectra were observed at 212 nm region which can be assign to π -π* transition of the aromatic rings, the second spectra are observed within the wavelength of 370 nm due to the transition between the n -π* (n-orbital localized on the central azomethine (CH=N-) bond), it can also be ascribed to entire charge transfer Schiff base molecules. These transitions existed also in the spectra of the complexes but shifted to 233 nm-250.03 nm and 361.90 – 345.25 for π - π* and n–π* transition respectively which shows the coordination of the Schiff base to metal ions (Ahmed and Kassem 2010).

Table 7: Microanalysis Data of the Schiff base and its Metal (II) Complexes

Compound	(Calculated)/Found (%)		
	C	H	N
$C_{13}H_{10}N_2S_2O_2$	(60.47) 62.51	(3.88) 3.51	(10.85) 11.04
$[MnL_2]\ .2H_2O$	(51.58) 51.19	(3.64) 3.42	(9.26) 9.51
$[FeL_2]\ .2H_2O$	(51.50) 51.71	(3.63) 3.59	(9.24) 9.43
$[CoL_2]\ .2H_2O$	(51.24) 51.42	(3.61) 3.73	(9.20) 9.30

L= $C_{13}H_9N_2SO_2$

The results of the elemental analysis of the Schiff base and the metal(II) complexes are presented in Table 7. It was observed that there was a very good agreement between the calculated percentage values of the C, H and N in the compound and the actual values found, which is also in good agreement with the proposed formulation of the compounds predicting 1:2 metal to ligand ratio.

Table 8: Antibacterial Activity of the Schiff base and its Metal (II) Complexes

Isolates	Compounds	Zone of Inhibition (mm)			Standard (mm)
		500µg/ml	1000µg/ml	2000µg/ml	500µg/ml
Staphylococcus Aureaus	$C_{13}H_{10}N_2S_2O_2$	10	12	15	Ciprofloxacin
	$[MnL_2]\ .2H_2O$	09	11	14	
	$[FeL_2]\ .2H_2O$	08	10	12	27
	$[CoL_2]\ .2H_2O$	10	12	16	
Eschericia coli	$C_{13}H_{10}N_2S_2O_2$	06	10	12	
	$[MnL_2]\ .2H_2O$	06	06	06	
	$[FeL_2]\ .2H_2O$	09	13	16	
	$[CoL_2]\ .2H_2O$	12	14	17	30

The *in-vitro* antibacterial activity of the Schiff base and its respective metal (II) complexes of (Mn(II), Fe(II), and Co(II) were tested against bacterial isolates, (*Staphylococcus aureus and Escheria coli)* using the disc diffusion method by taking DMSO as solvent at a concentration of 2000 µg/ml, 1000 µg/ml and 500 µg/ml, ciprofloxacin were used as a control. The zone of inhibition was measured for both disc, the results were compared with those of the standard drug ciprofloxacin. The Schiff base shows moderate activity against bacterial isolate in the range (06-18) mm zone of inhibition, with the highest activity of 15mm against *Staphylococcus aureaus,* at 2000µg/ml and the lowest activity of (06 mm) against *Escheria coli* at 500 µg/ml. The activity increases with the increase in concentration. The metal(II) complexes exhibit relatively higher antibacterial activity than that of the Schiff base; this is probably due to chelation in the metal complexes. The activities increased with the increase in concentration against all bacterial isolates except Mn(II) complex which was found to be inactive (06 mm) against *Escheria coli* at all concentrations 2000 µg/ml, 1000 µg/ml and 500 µg/ml, (Table 8).

Table 9: Antifungal Activity of the Schiff base and its Metal (II) Complexes

Isolates	Compounds	Zone of Inhibition (mm)			Standard(mm)
		500µg/ml	1000µg/ml	2000µg/ml	500µg/ml
Aspergillus Niger	$C_{13}H_{10}N_2S_2O_2$	11	13	17	Ketoconazole
	$[MnL_2]\ .2H_2O$	06	09	12	
	$[FeL_2]\ .2H_2O$	12	16	18	25
	$[CoL_2]\ .2H_2O$	13	16	18	
Candida albicans	$C_{13}H_{10}N_2S_2O_2$	08	09	13	
	$[MnL_2]\ .2H_2O$	08	10	13	
	$[FeL_2]\ .2H_2O$	06	10	14	
	$[CoL_2]\ .2H_2O$	09	11	15	31

L=$C_{13}H_9N_2SO_2$

Antifungal studies were carried out by disc diffusion technique on potato dextrose agar against *Aspergillus niger*, and *Candida albicans*, using Ketoconazole as control. The data revealed that the Schiff base and the metal complexes shows an appreciable activity against all the isolates. The Schiff base was found to be active at all concentration 2000 µg/ml, 1000 µg/ml and 500µg/ml, against the tested species with the highest activity of 17mm zone of inhibition at concentration of 2000 µg/ml against *Aspergillus niger*, and the lowest activity of 08mm at a concentration of 500 µg/ml against *Candida albicans*. The complexes also show an appreciable activity at a range of (06-18) mm zone at all concentrations. Fe(II) complex exhibit higher activities at (18 mm) at a concentration of 2000 µg/ml against *Aspergillus niger*. The activity increases with an increase in concentration against all isolates (Table 9).

CONCLUSION

Schiff base, 2-((4-nitrobenzylidene)amino)benzenethiol, was synthesized by the condensation of 2-aminobenzenethiol and 4- nitrobenzaldehyde in ethanol, and possessed a melting point of 160 ^oC. The decomposition temperature of the metal complexes ranges from (222 ^oC-232 ^oC), showing that the metal complexes are more stable than the Schiff base, the complexes synthesized containing 1:2 metal-to-ligand ratio and were found to be stable, non-electrolyte with Square-planner geometry. Antibacterial studies of the Schiff base and its metal(II) complexes revealed that the metal complexes show better activity when compared to that of the Schiff base.

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