Vol. 1 No. 2, December 2021

FUAM Journal of Pure and Applied Science

Available online at
www.fuamjpas.org.ng

An official Publication of
College of Science
Joseph Sarwuan Tarka University,
Makurdi.

FUAM Journal of Pure and Applied Science
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https://fuamjpas.org.ng/
Vol.1. No. 2. December, 2021

Synthesis, Characterization and Nematicidal Studies of Cu^{2+} and Fe^{2+} Complexes of Schiff Base Derived from 2-Phenylglycinemethylesterhydrochloride and Benzaldehyde

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Received: 28/10/2021 **Accepted**: 26/11/2021 **Published online**: 03/12/2021

Abstract

The Schiff base ligand N-diphenylamineacetate (DMA) was prepared by reacting 2-phenylglycinemethylesterhydrochloride and benzyladehyde which was used to synthesize transition metal complexes of Cu (II) and Fe (II). The process was achieved by the use of microwave oven assisted synthesis regulated at 100 ^{O}C for 30 minutes. The ligand and complexes were characterized on the basis of physical properties, FTIR, UV, XRD and Magnetic Susceptibility measurements. Results from the FTIR spectra of the ligand and complexes showed complexation with coordination through the nitrogen of the azomethine group. The results from UV and magnetic susceptibility confirmed the probable tetrahedral geometries of Cu (II) and Fe (II) complexes. Cell dimensions of a (4.7Å), b (15Å), c(5Å) , α (90^{O}), β (90^{O}) and γ (90^{O}) for Fe (II) complex are in agreement with orthorhombic crystal system. The complexes were found to be electrolytic in alcohol. The nematicidal activities of the metal complexes shows higher inhibiting potentials compared to the uncomplexed ligand in the root knot nematode *Meloidogyne incongnita* present in the crop *Esculentum spp.*

Keywords: Nematicidal activity, 2-phenylglycinemethylesterhydrochloride, Benzyaldehyde, *Meloidogyne incognita.*

Introduction

The study of the interaction of metal ions with organic ligands has gained influence as they have been shown to possess better antimicrobial activity compared to free ligand (uncomplexed). These types of reactions have been greatly harnessed in the investigation of mechanistic pathways in the synthesis of new drug. The synthesis of novel coordination compounds is a likely step toward generating new ideas of evaluating antimicrobial activity. In recent time, there has been a renewed interest in synthesis and study of Schiff bases. This may be attributed to their wide spectrum of biological and industrial applications [1-3]. A number of reports have appeared in literature highlighting the use of metal complexes of Schiff bases as having higher activities against microorganism compared to free ligands achieved through chelation [4]. The chelation has the tendency to reduce the polarity which then increases the lipophilicity of the metals complexes and eventually allows the penetration of the complexes across the membranes and blocks the active sites which the microbes are supposed to occupy [5-7]. The formation of Schiff bases from aldehyde or ketone is a reversible reaction and normally occurs in the presence of an acid or base catalyst or upon heating. This reaction is generally driven to the complexion by separation of the product or removal of water or both. Schiff bases have been employed as intermediates for the synthesis of amino acids or as ligands for the synthesis of metal complexes with different structural variety [8].

Many Schiff base complexes of metal ions have demonstrated high catalytic activity in synthetic processes including polymerization reactions and ring closure. The resistance of nematodes and other microbes to the previously used drugs has raised a global concern. This has triggered research for new drugs with relatively higher efficiency that can fit into the binding sites and combat the ravaging effects of these organisms. A considerable number of research finding have been reported on the synthesis, structural elucidation and biocidal studies of different types of Schiff bases and their metal complexes, but few data is available on the synthesis, characterization and nematicidal studies of Schiff base complexes derived from 2-

phenylglycinemethylesterhydrochloride and Benzyaldehyde, as data obtained from this work will elucidate the effects of nematodes on agricultural crops [5].

Materials and Methods

All the chemicals and solvents used for the synthesis were of analytical grade and purchased from BDH and Merck Chemical Co. They were used without further purification. The infrared spectra of the ligands and metal complexes were run as KBr discs in the range 4000-450 cm^{-1} on a *Shimadzu* infrared spectrophotometer.

Preparation of N-diphenylaminemethyleneacetate

The synthesis of N-diphenylaminemethyleneacetate was carried out in accordance with the method described by Iorungwa *et'al* [9]. Exactly 3.3 g (0.01 mmol) of 2-phenylglycinemethylester hydrochloride accurately weighed into a crucible and pulverized into fine powder and 2.2 g of benzylaldehyde and 10 mL of absolute ethanol added. The mixture was stirred together with 2.78 g of triethylamine for 1 h and placed in a thermostated microwave oven DHG-9101-ISA PEC medical USA model and power source of 220V for 30 minutes with continued stirring. The temperature of the oven was maintained at 100 ◦C. The temperature was monitored using a thermocouple device. A milky coloured solid product formed was filtered, washed with ethanol, dried on the water bath for 30 minutes and preserved in a refrigerator.

Synthesis of complexes

Using a 250 mL beaker, 5.0 (0.01 mol) of Schiff base ligand and 20 mL ethanol was added drop wise into 1.0 mmol of metal salts of Cu(II) chloride and Fe(II)chloride, respectively. Each mixture was stirred thoroughly and placed into a microwave oven for 30 minutes. Each metal complexes formed were filtered, washed with distilled water. The final product formed was air-dried and preserved in a refrigerator at 50 ◦C.

Results and Discussion

The synthesized compounds were crystalline, coloured and soluble in water, acetone, DMF, DMSO, methanol and ethanol.

Table 1: Some physical characteristics of ligand and complexes

Ligand/Complex	Molecular Formula	Molecular Weight(g)	Colour	Yield (%)	pH
DMA	$C_{16}H_{15}O_2N$	253	Milky	78.7	6.3
DMA-Cu	$[Cu(C_{16}H_{15}O_2N)Cl_2].2H_2O$	423.48	Light blue	20.9	4.7
DMA-Fe	$[Fe(C_{16}H_{15}O_2N)Cl_3].4H_2O$	451.93	Light brown	5.6	3.3

Table 2: Electronic spectral data for ligands/complexes

Ligand/complex	λ_{max}(nm)	λ max(cm^{-1})	Assignment	Geometry
DMA	258	38.759	π-π*transition	-
	269	37.174		
DMA-Cu	228	43.859	π-π*	Tetrahedral
	268	37.313		
DMA-Fe	267	37.545	-	Tetrahedral

Table 3: Unit cell parameters for synthesized ligand and complexes

S/No	Ligand/Complexes	Unit Cell Parameters			Vol.(cm^3)	Crystallite Size (nm)	Crystal Structure
		a(Å)	b(Å)	c(Å)			
1	DMA	4.1	3.85	4.7	75.15	81.53	Orthorhombic
2	DMA-Fe	4.7	15	5.0	352.5	86.06	Orthorhombic
3	DMA-Cu	-	-	-	-	-	-

Infrared spectral studies

The electronic spectral studies of the ligands DMA and their metal complexes have been recorded in methanol. The spectronic studies of the DMA ligand and its complexes showed absorption bands at 258 nm and 269 nm assignable to the π-π* transition. At lower energy, DMA ligand showed absorption band assigned to the π-π* transition. Upon complexation, the bands shifted to 267 nm in the DMA-Fe complex, as a result of the metal ligand interaction [9-11].The DMA-Cu complex had bands at 228 nm. Other bands occurred at 268 nm assigned to a π-π* transition.

FTIR characterization

The infrared spectral for the ligand and synthesized complexes were recorded using KBr pellets in the range of 4000-450 cm^{-1} and provided valuable information regarding the nature of the functional groups attached to the metal ion. The comparison of the IR spectral of the synthesized ligand and metal complexes reveals the binding mode of the ligands to the metal ion which is confirmed by the shift in the positions of the absorption peaks. The IR spectral of the DMA ligand showed a broad band around 1576 cm^{-1} which can be attributed to ν(C=N)and shifted hypsochromically in the range 1587 cm^{-1} in the complex indicating the imine nitrogen involvement in the coordination to the metal ion. This is further supported by the appearance of the medium band at 898 cm^{-1}assigned to ν(M-N) vibration. A medium intensity band in the region of 3600-3640 cm^{-1} assigned to the phenolic and H_2O group whose positive shift is attributed to the coordinated water molecule. The band characteristic of ν(C=O) appeared at 1494 cm^{-1} and undergoes a blue shift to 1442 cm^{-1} whereas the band at 3347 cm^{-1} is attributed to the NH stretching. In addition, the complex showed bands at 700 cm^{-1} and 898 cm^{-1}further confirming formation of coordination complexes. These observations agree with the findings from previous research [12]. In the DMA-Cu complex, the absorption bands appeared in the regions of 3332 cm-1, 1576 cm^{-1}, 916 cm^{-1} and 670 cm^{-1} implying coordinated water molecules, complexation of the metal atoms to the Schiff base through formation of M-N, and M-O bonds respectively [13]. The relevant spectral in the DMA-Fe complex appeared at 1576 cm^{-1}, 3369 cm^{-1} and 1490 cm^{-1} attributed to the azomethine linkage, in the complex formation of coordination complex through M-N interaction and M-O bonds [14].

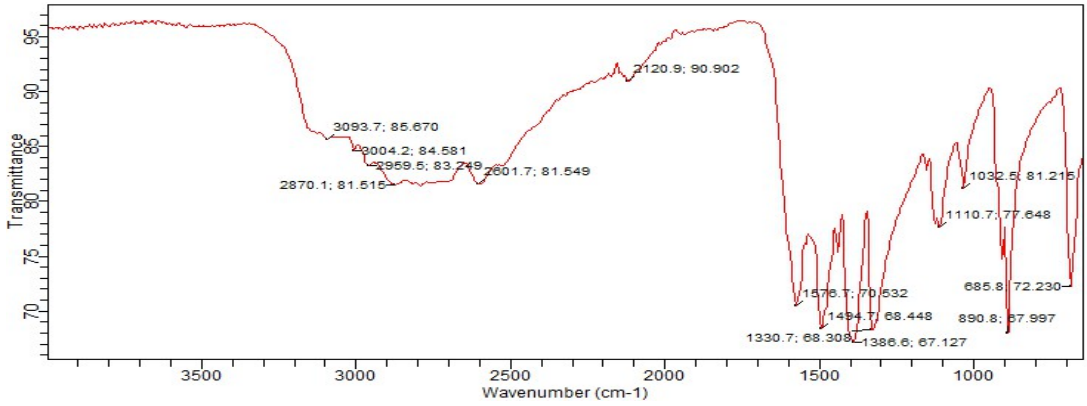

Figure 1: FTIR spectrum of DMA ligand

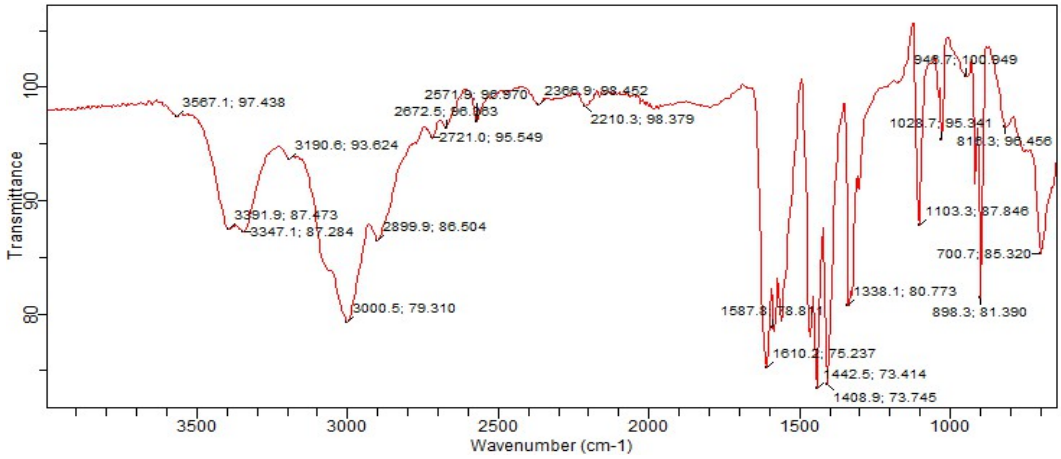

Figure 2: FTIR spectrum of DMA-Cu complex

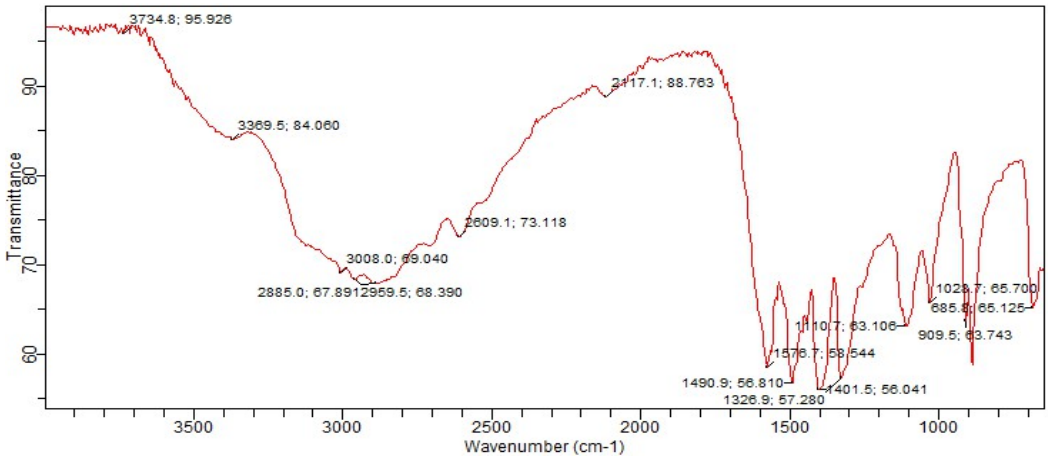

Figure 3: FTIR Spectrum of DMA-Fe Complex

X-Ray Diffraction (XRD) Characterization

X-ray power diffraction characterization of the synthesized Schiff bases and their metal complexes were carried out in Umaru Musa Yar'adua University, Katsina State Nigeria in the Central Research Laboratory with X-ray Diffractometer (Thermo Scientific Model ARL X TRA X-ray 197492086). The unit cell parameters for synthesized ligands and metal complexes are as presented in Table 4.

TABLE 4: X-Ray Diffraction data of $[Fe(C_{15}H_{14}O_2N_2)Cl_3].4H_2O$ Complex

S/No	d-Spacing (Å)		2θ values		Δ2θ	hkl
	Observed	Calculated	Observed	Calculated		
1	5.03108	5.02479	8.8145	8.8008	0.0137	110
2	4.40355	4.39824	10.0829	10.0670	0.0159	111
3	3.96661	3.96172	11.2072	11.1921	0.0151	020
4	3.71597	3.71137	11.9739	11.9583	0.0156	200
5	3.51278	3.50861	12.6777	12.6561	0.0216	020
6	2.99079	2.98715	14.9378	14.9158	0.0220	211
7	1.97176	1.96941	23.0161	22.9856	0.0305	320
8	1.82942	1.82719	24.9237	24.8851	0.0386	030
9	1.62941	1.62742	28.2384	28.2032	0.0352	311
10	1.26296	1.26142	37.6201	37.5605	0.0596	300

TABLE 4: X-Ray Diffraction data of $[Cu(C_{16}H_{15}O_3N)Cl_2].2H_2O$ Complex

S/No	d-Spacing (Å)		2θ values		Δ2θ	hkl
	Observed	Calculated	Observed	Calculated		
1	5.95315	5.94594	7.4408	7.4291	0.0117	100
2	5.36917	5.36286	8.2554	8.2446	0.0108	100
3	4.21964	4.21455	10.5272	10.5095	0.0177	010
4	3.98870	3.98385	11.1443	11.1279	0.0164	011
5	3.34043	3.33636	13.3436	13.3265	0.0171	111
6	3.20087	3.19701	13.9369	13.9160	0.0209	111
7	3.04579	3.04215	14.6619	14.6432	0.0187	200
8	2.68698	2.68376	16.6734	16.6432	0.0249	220
9	2.58532	2.58224	17.3494	17.3255	0.0239	220
10	2.50754	2.50455	17.9055	17.8785	0.0270	211

The XRD pattern indicated a crystalline nature for the ligands and its metal complexes. Indexing of the diffraction pattern was performed by using the trial and error method. The Miller indices (hkl) along with observed and calculated 2θ angles, the observed and calculated d values are presented in Tables 3 and 4. The result shows that the ligand and its metal complexes have orthorhombic structure. The findings from this research were compared with those obtained by Atagher [5] and it was in close agreement. The XRD spectral data are as presented in Figures 4 and 5 and 6. Additionally, using the diffraction data, the mean crystallite sizes of the ligands and complexes D was determined according to the Scherrer's equation

$$(D=\frac{0.9\lambda}{\beta Cos\ \theta}). \qquad (1)$$

Where λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle and β is the full width at half maximum of diffraction peak.

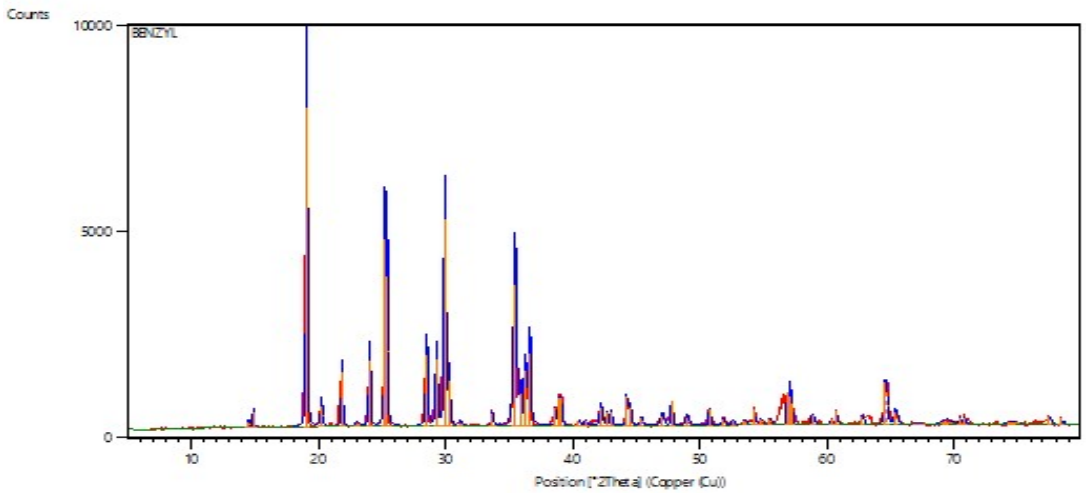

Figure 4: XRD Diffractogram of (DMA) Schiff base Ligand

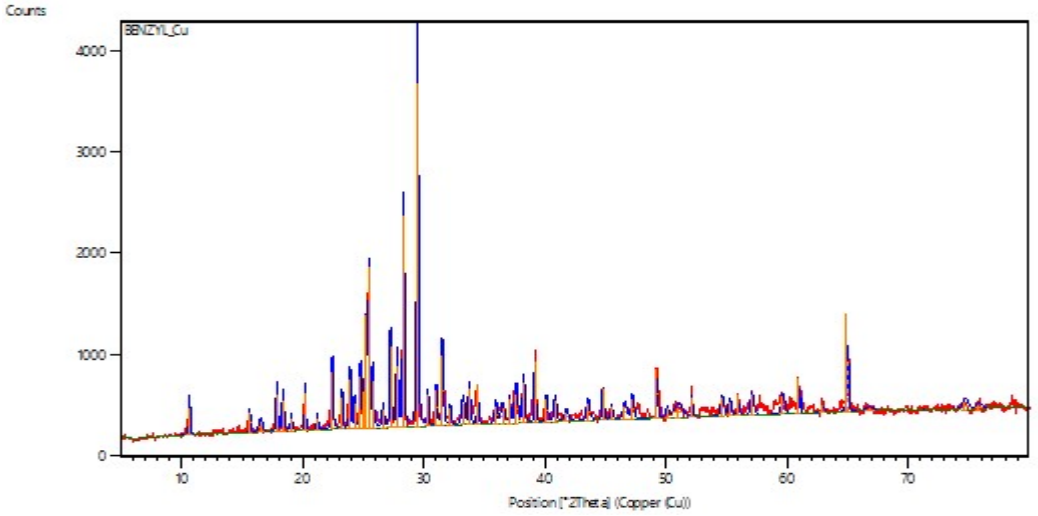

Figure 5: XRD Diffractogram of DMA-Cu

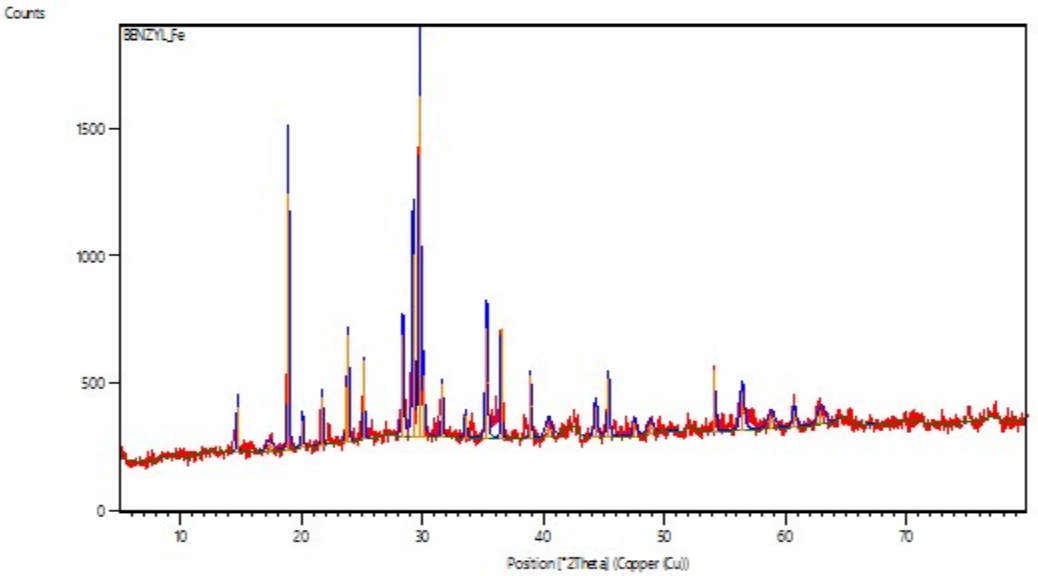

Figure 6: XRD diffractogram of DMA-Fe

UV/Vis spectral characterization

The spectronic studies of the DMA ligand and its complexes showed absorption bands at 258 nm and 269 nm assignable to the π-π* transition. At lower energy, DMA ligand showed absorption band assigned to the π-π* transition. Upon complexation, the bands shifted to 267 nm in the DMA-Fe complex, as a result of the metal ligand interaction. The DMA-Cu complex had bands at 228 nm. Other bands occurred at 268 nm assigned to a π-π* transition. The spectral data is as presented in Figures 7, 8 and 9. The UV-visible absorption spectral studies of the ligands and their metal complexes showed similarities as an indication of the similarities in their structures and geometry. In the complexes, there were notable changes in both frequencies and intensities in the characteristic bands of the complexes compared to free ligands. The blue shifts and hypsochromic shifts observed in the absorption bands during complex formation indicate coordination of the ligands to the metal ion. These observations are in complete agreement with those of Atagher [5].

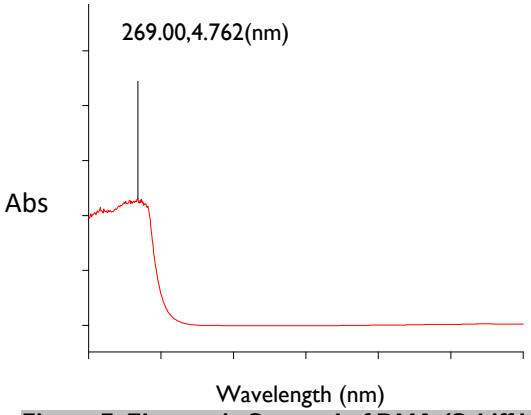

Figure 7: Electronic Spectral of DMA (Schiff base) Ligand

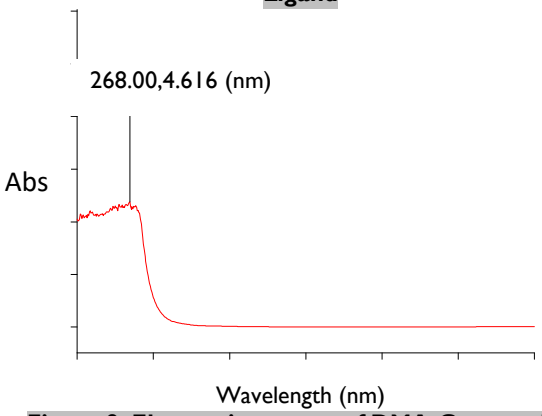

Figure 8: Electronic spectra of DMA-Cu complex

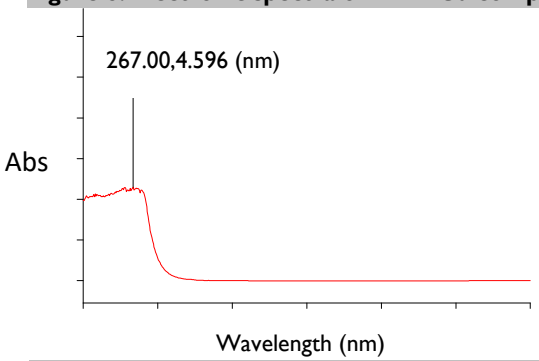

Figure 9: Electronic spectra of DMA-Fe complex

Evaluation of Nematicidal activity of root Knot Nematodes (Meloidogyne Incognita)

The synthesized ligands DMA, and their metal complexes of Cu, and Fe were tested for mortality against the root knot nematodes (*Meloidogyne Incognita*) at three different concentrations which include 2.5, 5.0 and 10.0 ppm.

This analysis was carried out within 25 h and observations were recorded every 5 h of exposure. In each of the treatment, exactly 10 juveniles were placed and their mortality rate observed, and their corrected percentage mortality rate calculated.

For DMA, the corrected mortality rate of 0 % was recorded at the concentration of 2.5 ppm at 5 hrs of exposure. Mortality of 22.2 % was recorded at concentration of 10 ppm. At a higher concentration of 10 ppm, the corrected percentage mortality of 55.8 % was recorded at 10 h of exposure. At 10 hrs of exposure, the corrected mortality rate of 0 % was observed at 2.5 ppm.

The corrected mortality of 66.7 and 77.8 were recorded at the concentrations of 5 ppm and 10 ppm respectively. At 15 h of exposure, percentage mortality of 33.3 % was recorded at concentration of 2.5 ppm, 77.8 % was recorded at concentration of 5 ppm while at concentration of 10 ppm, a corrected mortality rate of 8.87 % was obtained.

The metal complex DMA-Cu at the first 5 h of exposure recorded a corrected percentage mortality of 100 % for all the concentrations. At 10 and 15 h of exposure, the same 100 % was observed at all concentrations. This implies that the efficiency of the Schiff base complex is not concentration and time dependent [9].

For the DMA-Fe complex, the corrected mortality rate of 22.2 % was recorded at the first 5 h of exposure at the lowest concentration of 2.5 ppm. 55.6 5 was recorded at 5.0 ppm whereas at 10 ppm, the corrected percentage mortality rate was 66.7 % at 10 h of exposure. The corrected percentage mortality of 22.2 % was also observed at a concentration of 2.5 ppm, but at a higher concentration of 5 ppm and 10 ppm, the corrected percentage mortality was 77.8 % and 88.9 % respectively. At 15 h of exposure, the corrected percentage of 55.6 % was obtained for the concentrations of 5 ppm and 10 ppm, the corrected percentage mortality was 100 %.

Table 4: Nematicidal activity of *Meloidogyne incognita* using the synthesized metal complexes and Schiff base ligands

S/No	Synthesized Compounds	No of hours	Mortality(%) at various concentrations		
			10:00 ppm	5:00 ppm	2.50 ppm
1	DMA	0	0	0	0
		5	55.6	22.2	0
		10	77.8	66.7	0
		15	88.7	77.8	33.3
		0	0	0	0
		5	0	0	0
Control		10	0	0	0
		15	0	0	0
2	DMA-Cu	0	0	0	0
		5	100	100	100
		10	100	100	100
		15	100	100	100
3	DMA-Fe	0	0	0	0
		5	66.7	55.6	22.2
		10	88.9	77.8	22.2
		15	100	100	55.6

From the results of the analysis, it was also observed that the metal complexes were more efficient than the ligand in terms of their reactivity. This result also agrees with other findings elsewhere [15-18]. This greater activity of the metal complexes is attributed to the azomethine linkage and the heteroatom present in these compounds [19].

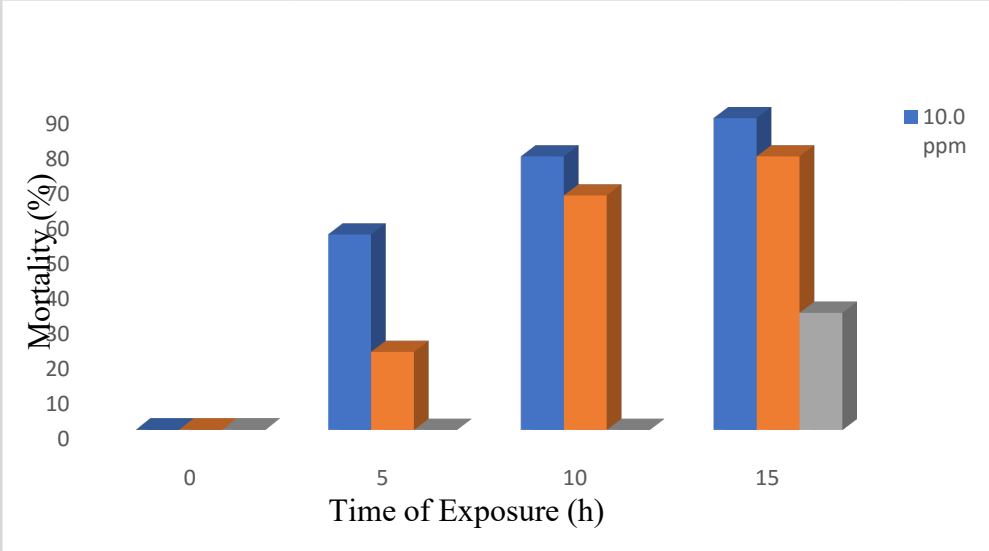

Figure 10: Corrected Percentage Mortality for the Ligand DMA

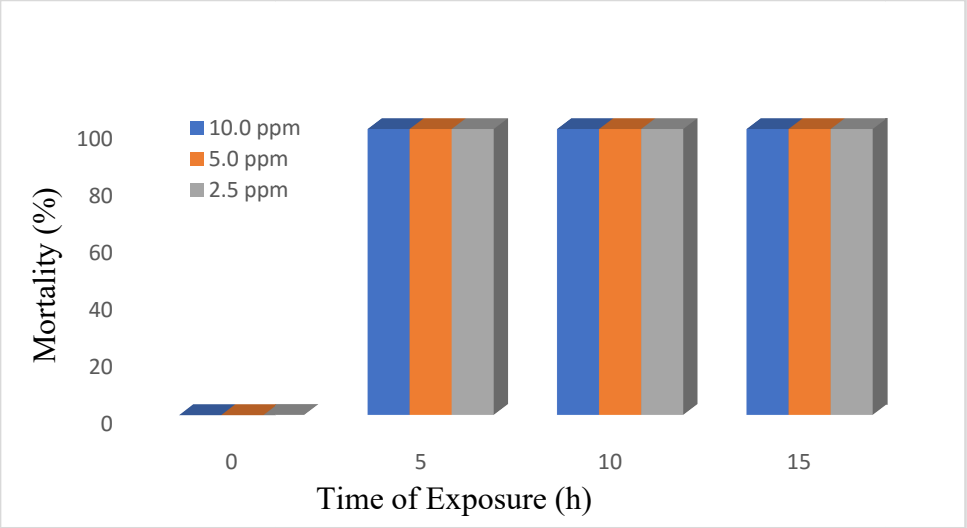

Figure 11: Corrected Percentage Mortality for the Complex DMA-Cu

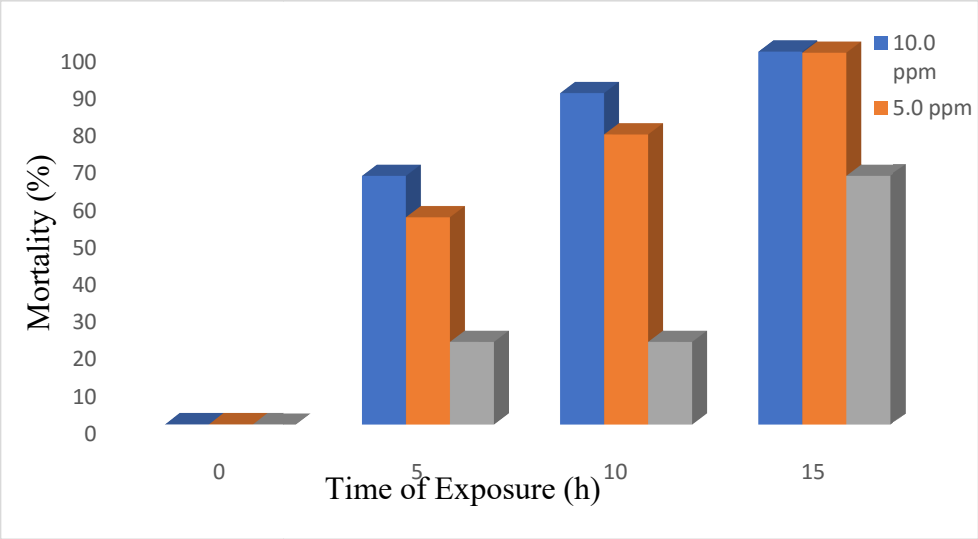

Figure 12: Corrected Percentage Mortality for the Complex DMA-Fe

Conclusion

This research work has achieved the synthesis and characterization and nematicidal studies of ligand and its metal complexes against the root knot nematode *meloidygyne incognita.*

The result showed that the metal complexes possessed higher inhibiting potential for the nematodes compared to the free ligands. It was also discovered that the efficacy of the complexes was higher than those of the ligands at the higher concentrations and time of exposure.

Declaration of conflicting interests

The authors declared no potential conflicts of interest.

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Cite this article

Iorungwa M.S., Wuana R.A., Chahul H.F., Atagher J.A. and Ona J.I. (2021). Synthesis, Characterization, and Nematicidal Studies of Cu^{2+} and Fe^{2+} Complexes of Schiff Base Derived from 2-Phenylglycinemethylesterhydrochloride and Benzaldehyde. FUAM Journal of Pure and Applied Science, **1**(**2**):99-109