©IDOSR PUBLICATIONS
International Digital Organization for Scientific Research ISSN: 2579-0781
IDOSR JOURNAL OF EXPERIMENTAL SCIENCES 3(1) 11-27, 2018.

Synthesis, Characterization and anti-Microbial Studies of Metal (II) Complexes with (E)-4-methoxy-N-(4-methoxybenzylidene) aniline

*[1]Abdullahi S. and [2]Na'aliya J.

[1]Department of Science Laboratory Technology, Federal Polytechnic, Mubi PMB 035 Adamawa State, Nigeria.

[2]Department of Pure and Industrial Chemistry,Faculty of Science, Bayero University, Kano State, Nigeria.

ABSTRACT

Some divalent transition metal complexes was synthesized by the reaction of the chlorides of Co(II), Fe(II), Mn(II), and Ni(II) with Schiff base derived from the reaction of 4-methoxybenzaldehyde with 4-methoxyaniline in methanolic solution. The Schiff base, L was obtained as grey crystals with melting point of 153°C. The metal(II) complexes were all coloured, ML melted in the range of 171-177°C. A conductivity measurement for the complexes in DMSO was in the range of 77.58-85.10 Ω^{-1}mo^{l-1}cm^{2}. Thelarge values for L suggest the presence of anion outside the coordination sphere. All the complexes were found to be paramagnetic as observed from the values of their magnetic moments and also soluble in most common solvents. The infra-red spectral analysis indicates complexation has taken place. The metal-ligand ratio in all the complexes was 1:2 from Job's method of continuous variation results. The percentage composition of the metals and their corresponding ligands were found from the complexes gravimetrically. The results obtained were in good agreement with the calculated values. The ligand and its corresponding complexes were screened in-vitro for antibacterial activity against some pathogenic bacteria: Escherichia coli, Aspergillus fumigatus, Salmonella typhi, Staphylococcus aureus, Aspergillus flavus and Mucor species using the paper-discs diffusion method. Inhibition properties of the complexes showed that the complexes have higher antimicrobial activity than the ligand which could be attributed to chelation.

Keywords: 4-methoxybenzaldehyde, 4-methoxyaniline, Schiff bases, antimicrobial activity

INTRODUCTION

Schiff bases are an important class of ligands derived from amino and carbonyl compounds that coordinate to metal ions via azomethine nitrogen and have been studied extensively. The C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [1].

Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities [2, 3]. Schiff-base complexes are considered to be among the most important stereo-chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [4].

Para-anisidine (*p*-anisidine) or 4-methoxyaniline, a grey-brown solid, is the most toxic of the three isomers of anisidine and causes blood damage upon oral ingestion, inhalation or skin contact [5]. *P*-anisaldehyde or 4-methoxy benzaldehyde is an organic compound (slightly yellow oily liquid) that occurs naturally in the fennel and anise plants. Herein is reported the synthesis, characterization and anti-microbial studies of metal (II) complexes with (E)-4-methoxy-N-(4-methoxybenzylidene) aniline derived from 4-methoxyaniline and 4-methoxybenzaldehyde

Materials and Methods

All the chemicals/reagents used throughout this work were of analar grade. They includes; 4-methoxybenzaldehyde, 4-methoxyaniline, ethanol, DMSO, P_2O_5 (phosphorus pentaoxide), methanol. The materials used includes, hot plate with magnetic stirrer, condenser and round bottom flask, beakers, conical flasks, funnel, filter papers.

Synthesis of the Schiff base ligand

The Schiff base was synthesized as previously described [6, 7, 8] with a slight modification. The Schiff base was synthesized by the condensation of 4-methoxybenzaldehyde (6mmol, 0.8169g) with 4-methoxyaniline (6mmol, 0.7389g), in a 30cm3 methanolic solution (1:1) molar ratio to give L. The mixture was refluxed for one hour after which it was cooled to room temperature. The product formed was filtered, washed with 3x5ml portions of ethanol and dried over anhydrous phosphorus pentaoxide in a desiccator.

Synthesis of the M (II) complexes

The complexes were synthesized by reacting with Metal (II) salt and the ligand in a 1:2 molar ratio. To a solution of the Schiff base ligands, L in 10ml methanol, 3mmol of CoCl2.6H2O, FeCl2.4H2O, MnCl2.4H2O or NiCl2.6H2O in 25ml methanol was added with constant stirring. The mixture was refluxed for 2 hours using a hot plate with magnetic stirrer, after which it was allowed to cool at room temperature and the product formed was filtered, washed with 3x5ml portions of methanol and stored in a desiccator containing anhydrous phosphorus pentaoxide.

Gravimetric determination of metals in the complex compounds

The samples were separately digested as described by [8] by weighing 0.2g of the desired metal complex into a 100cm^3 beaker containing 25cm^3 of distilled water and 5cm^3 of concentrated nitric acid (HNO_3, specific gravity 1.42g/cm^3). The mixture was heated to about dryness and the contents of the beaker were allowed to cool to room temperature after which 25cm^3 of distilled water was added. The mixture was stirred, filtered and the filtrate collected and used for their determinations.

Determination of Manganese as $Mn(NH_4)PO_4.H_2O$

Distilled water was added to the filtrate obtained from the digested manganese (II) complex compound and made up to the mark in a 100cm^3 volumetric flask with more distilled water. The solution was transferred to a 250cm^3 conical flask and dilute ammonia solution was added to neutralize the filtrate after which 10g of ammonium chloride, excess diammonium hydrogen phosphate $(NH_4)_2HPO_4$ and some few drops of (1:3) hydrochloric acid were added respectively. The mixture was heated to 95°C followed by drop wise addition of dilute aqueous ammonia solution with constant stirring until a precipitate of $[Mn_3(PO_4)_2]$ began to form. The addition of ammonia solution was stopped immediately while heating and stirring continued in order to ensure that the precipitation of$MnNH_4PO_4.H_2O$. The beaker and its contents were allowed to cool to room temperature. The precipitate was filtered, washed with 1% ammonium nitrate solution and the product heated to a constant weight. It was weighed as $MnNH_4PO_4.H_2O$, [8].

Determination of Iron as Fe_2O_3

Iron was determined by adding ammonia solution (6M) to the hot solution of the complex with constant stirringuntil the solution was slightly basic (this was indicated by a pH probe). The probe was rinsed back into the beaker before removing it so as to not lose any iron. The precipitate was digested by boiling for 5 minutes (by flocculation) and allowed to settle. The solution was stirred and filtered. The precipitate was washed with hot 1% NH_4NO_3. A small volume of the filtrate was transferred into a beaker and few drops of 0.1M $AgNO_3$ added to test for completion of precipitation which was indicated by non-formation of a white precipitate. The precipitate was filtered using a filter paper which was folded and burnt in a crucible at red heat for 15minutesto obtain the Fe_2O_3 residue. Once the sample has been ignited, the crucible was cooled completely before its mass was accurately measured [9].

Determination of Cobalt as $Co[Hg(SCN)_4]$

4.8ml of mercury (II) chloride solution was added to the solution of the complex with constant stirring followed by addition of 5.5cm^{3}ammonium thiocyanate solution for 1 – 3 minutes, a dark-blue precipitate was formed. Stirring was continued for a further 3 minutes before the solution was allowed to stand for2 hours at room temperature. The precipitates formed were collected in aweighed sintered glass (porosity no.4), washed with 3cm^3 of a dilute solutionof ammonium thiocyanate and finally with 5cm^3 ice-cold water. It was then dried at 100C and weighed as $Co[Hg(SCN)_4]$ [8].

Determination of Nickel as Ni $(HDMG)_2$

0.35g of pure ammonium nickel sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$ was weighed and dissolved in 25cm^3 water contained in 500cm^3 beaker. 5cm^3 of HCl (1:1) was added and then diluted to 200cm^{3}with more distilled water before heated to 80ºC, a slight excess ofdimethylglyoximate (DMG) solution was added to the solution immediately followed by drop wise addition of dilute ammonia solution with constant stirring until precipitation took place. The mixture was allowed to stand on a steam bath for 30 minutes for the red DMG-nickel complex to settle down. The precipitate was allowed to stand for another 60 minutes to cool to the room temperature. The cold solution was filtered through a sintered-glass previously heated to 120°C. The precipitates was washed with cold water until free from chloride ions and dried at 110°C for 50 minutes. It was then allowed to cool in a desiccator and reweighed until a constant weight was achieved. It wasweighed finally as$Ni(C_4H_7O_2N_2)_2$ [8].

Determination of Chloride as [AgCI]

The percentage of chlorine in the sample was determined by weighing about 0.2g of the complex into a 250cm^3beaker with astirring rod and covered with a watch glass. Then about 150 cm^3 of water and 0.5cm^3 of concentrated nitric acid were added to the complex and stirred until the solids dissolved. 0.1M of silver nitrate solution was added slowly to the cold solution of the complex with constant stirring. The determination was done in a dark environment. The mixture was heated to nearly boiling temperature with constant stirring until the precipitate formed coagulated and the supernatant liquid was clear (between 2-3 minutes). Few drops of 0.1M silver nitrate solution were added to the supernatant as a confirmatory test to check for complete precipitation (absence of further precipitates confirmed the end of the test). The beaker with its content was kept in the dark and allowed to cool for 1 hour before filtration. A sintered glass filtering crucible (no. 4) was washed, dried (at 130°C) and cooled in a desiccator was weighed separately. The precipitates were washed 3 times with about 30cm^3 of cold and very dilute nitric acid (0.5cm^3 of the concentrated acid was dissolved in200cm^3 of water) and collected in the weighed crucible. The precipitate was washed again in the crucible with cold and very dilute nitric acid (0.05M) until 5cm^3 of the washings collected in a test tube gave no turbidity when two drops of 0.1M hydrochloric acid was added to it. The crucible with its contents were placed in an oven and dried at 140°C for 60 minutes before it was finally cooled in a desiccator and weighed as AgCl. The heating and cooling was repeated until a constant weight was attained. The percentage of chlorine in the sample was then calculated [9, 10].

Antibacterial Activity

The ligand and its complexes were dissolved separately in DMSO to have five different concentrations (Table 7a-b). They were placed on the surface of the culture and incubated at 37°C for 24hrs; the diameter of the zone of inhibition surrounding the disc was taken as the measure of inhibitory power of the compound against a particular test organism.

RESULTS AND DISCUSSION

Table 1: Physical properties of the ligand and itscomplexes

Compounds	Formular	Formular weight (g)	Colour	Yield (%)	M.pt (°C)
L	**$C_{15}H_{15}NO_2$**	**241.28**	**Grey**	**84.64**	**153**
CoL	**[CoL_2]**	**541.50**	**Yellow**	**84.94**	**171**
FeL	**[FeL_2]**	**538.41**	**Brown**	**83.42**	**176**
MnL	**[MnL_2]**	**537.51**	**Yellow**	**90.87**	**174**
NiL	**[NiL_2]**	**541.26**	**Green**	**89.20**	**177**

Key: L = $C_{15}H_{15}NO_2$

Table 2: Infrared Spectral and Gravimetric data of theligand and their complexes

Compound	*v* C=N	*v* M-N	*v* M-O	*v* $O\text{-}CH_3$	% metal in the complexes Calculated	Observed
L	1623			2942		
CoL	1610	645	536	2939	10.88	10.96
FeL	1620	644	533	2943	10.37	10.44
MnL	1623	632	537	2940	10.22	10.30
NiL	1620	637	537	2943	10.84	10.93
Key:	L = $C_{15}H_{15}NO_2$					

Table 3: Molar conductivity of the Schiff base complexes

Compound	Concentration, C (mol)	Specific conductance (S)	Molar conductance ($\Omega^{-1}mol^{-1}cm^2$)
CoL	1×10^{-3}	2.58×10^{-6}	2.58
FeL	1×10^{-3}	2.10×10^{-6}	2.10
MnL	1×10^{-3}	1.95×10^{-6}	1.95
NiL	1×10^{-3}	1.55×10^{-6}	1.55

Key: L = $C_{15}H_{15}NO_2$

Table 4: Magnetic Susceptibility of the complexes

Compounds	Gram susceptibility, Xg erg c^{-2} g^{-1}	Molar susceptibility, Xm	Effective magnetic moment (μeff) B.M
CoL	1.62×10^{-5}	8.75×10^{-3}	4.62
FeL	2.04×10^{-5}	1.10×10^{-2}	5.17
MnL	1.67×10^{-5}	8.96×10^{-3}	4.68
NiL	2.18×10^{-5}	1.20×10^{-2}	5.34
Key:	L = $C_{15}H_{15}NO_2$		

Table 5a: Job's method of continuous variation results of the metal(II) complexes

Co(II) Complex (λmax = 681.63nm)		Fe(II) Complex (λmax = 421.24nm)		Mn(II) Complex (λmax = 900.60nm)		Ni(II) Complex (λmax = 420.87nm)	
XL	Abs	XL	Abs	XL	Abs	XL	Abs
0.0830	0.1174	0.0830	0.1521	0.0830	0.0899	0.0830	0.1790
0.1670	0.2243	0.1670	0.1722	0.1670	0.1034	0.1670	0.2483
0.2500	0.2798	0.2500	0.1828	0.2500	0.1202	0.2500	0.2648
0.3330	0.3394	0.3330	0.1998	0.3330	0.1364	0.3330	0.3201
0.4170	0.3906	0.4170	0.2201	0.4170	0.1497	0.4170	0.3506
0.5000	0.4425	0.5000	0.2446	0.5000	0.1672	0.5000	0.4011

X_L = Mole fraction; Abs = Absorbance

Table 5b (cont): Job's method of continuous variation results of the metal (II) complexes

Co(II) Complex		Fe(II) Complex		Mn(II) Complex		Ni(II) Complex	
(λmax = 681.63nm)		(λmax = 421.24nm)		(λmax = 900.60nm)		(λmax = 420.87nm)	
XL	Abs	XL	Abs	XL	Abs	XL	Abs
0.5830	0.5021	0.5830	0.2622	0.5830	0.1882	0.5830	0.4535
0.6670	0.5716	0.6670	0.2898	0.6670	0.1984	0.6670	0.4901
0.7500	0.4515	0.7500	0.2481	0.7500	0.1721	0.7500	0.3255
0.8330	0.2719	0.8330	0.1921	0.8330	0.1501	0.8330	0.2309
0.9170	0.1009	0.9170	0.1525	0.9170	0.1172	0.9170	0.1089

X_L = Mole fraction; Abs = Absorbance

Table 6: Solubility of the ligand/complexes in water and some common organic solvents

Solvents	L	CoL	FeL	MnL	NiL
Acetone	S	S	S	S	S
CCl4	S	IS	SS	SS	SS
Chloroform	S	S	S	S	S
Diethylether	IS	S	S	S	S
DMF	S	S	SS	S	S
DMSO	S	S	S	S	S
Ethanol	IS	IS	IS	IS	IS
Formaldehyde	IS	IS	SS	IS	IS
Acetic acid	S	S	S	S	S
Methanol	IS	IS	IS	IS	IS
Pet. Ether	IS	IS	IS	SS	IS
Water	IS	IS	IS	IS	IS

Key: L = $C_{15}H_{15}NO_2$ IS = Insoluble S = Soluble SS = slightly soluble

Table 7a: Antibacterial activity of the ligands/complexes

Compound	Organism	Concentration (µg)/Zone of inhibition (mm)					
		5000	400	3000	2000	1000	Control (mm)
L	S. *aureus*	11	09	07	NZI	NZI	28 (Ampiclox)
L	E. *coli*	08	07	04	NZI	NZI	31 (Ampiclox)
L	S. *typhi* NZI	NZI	NZI	NZI	NZI	34 (Ampiclox)	
L	A. *fumigatus*	NZI	NZI	NZI	NZI	NZI	28 (Ketoconazole)
L	A. *flavus*	NZI	NZI	NZI	NZI	NZI	25 (Ketoconazole)
L	Mucor. *s*	NZI	NZI	NZI	NZI	NZI	33 (Ketoconazole)
CoL	S. *aureus*	11	09	07	NZI	NZI	28
CoL	E. *coli*	10	09	06	NZI	NZI	31
CoL	S. *typhi* 10	08	07	05	NZI	34	
CoL	A. *fumigatus*	08	06	05	03	NZI	28 (Ketoconazole)
CoL	A. *flavus*	NZI	NZI	NZI	NZI	NZI	25 (Ketoconazole)
CoL	Mucor. *s*	NZI	NZI	NZI	NZI	NZI	33 (Ketoconazole)
FeL	S. *aureus*	09	07	05	NZI	NZI	28(Ampiclox)
FeL	E. *coli*	10	08	07	NZI	NZI	31(Ampiclox)
FeL	S. *typhi* 11	10	07	NZI	NZI	34(Ampiclox)	
FeL	A. *fumigatus*	NZI	NZI	NZI	NZI	NZI	28 (Ketoconazole)
FeL	A. *flavus*	NZI	NZI	NZI	NZI	NZI	25 (Ketoconazole)
FeL	Mucor. *s*	NZI	NZI	NZI	NZI	NZI	33 (Ketoconazole)
MnL	S. *aureus*	NZI	NZI	NZI	NZI	NZI	28(Ampiclox)
MnL	E. *coli*	NZI	NZI	NZI	NZI	NZI	31(Ampiclox)
MnL	S. *typhi* NZI	NZI	NZI	NZI	NZI	34(Ampiclox)	
MnL	A. *fumigatus*	NZI	NZI	NZI	NZI	NZI	28 (Ketoconazole)
MnL	A. *flavus*	NZI	NZI	NZI	NZI	NZI	25 (Ketoconazole)
MnL	Mucor. *s*	NZI	NZI	NZI	NZI	NZI	33 (Ketoconazole)
NiL	S. aureus	12	10	07	NZI	NZI	28 (Ampiclox)
NiL	E. coli	10	08	07	NZI	NZI	31 (Ampiclox)

Key: L = $C_{15}H_{15}NO_2$ NZI = No zone of inhibition Ampiclox = (500mg per disc)

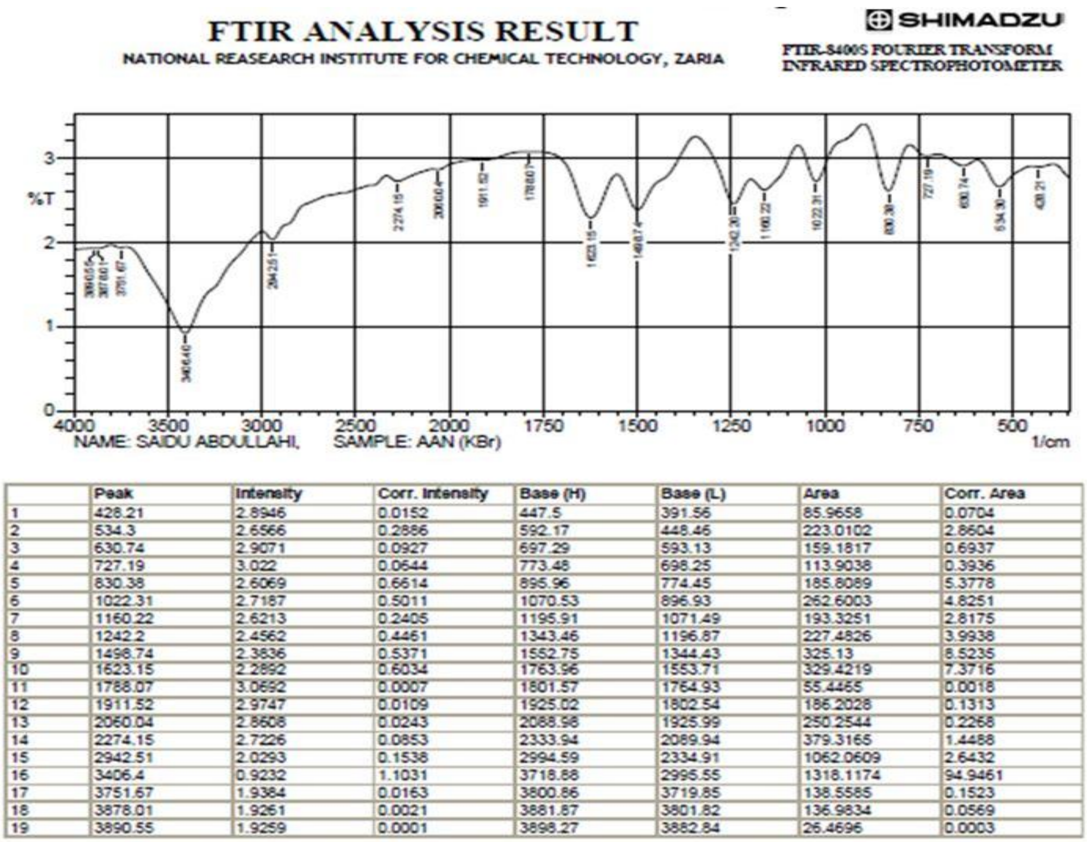
Ketoconazole = (200mg per disc)

Table 7b (cont): Antibacterial activity of the ligands/complexes

Compound	Organism	Concentration (μg)/Zone of inhibition (mm)					
		5000	400	3000	2000	1000	Control (mm)
NiL	S. typhi	10	08	07	NZI	NZI	34 (Ampiclox)
NiL	A. fumigatus	09	07	03	NZI	NZI	28 (Ketoconazole)
NiL	A. flavus	NZI	NZI	NZI	NZI	NZI	25 (Ketoconazole)
NiL	Mucor. S	NZI	NZI	NZI	NZI	NZI	33 (Ketoconazole)

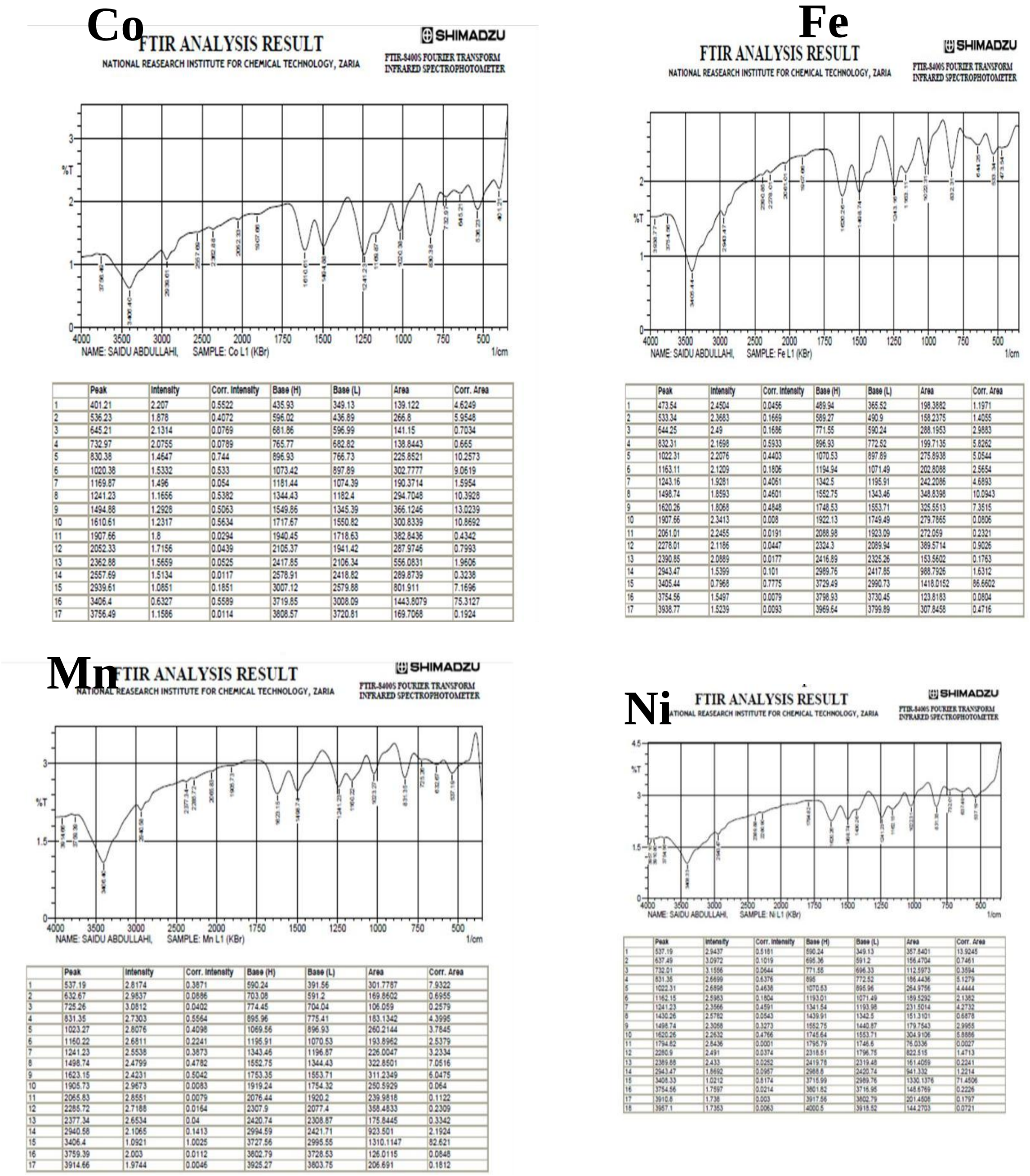
Key: L = $C_{15}H_{15}NO_2$ NZI = No zone of inhibition Ampiclox = (500mg per disc) Ketoconazole = (200mg per disc)

Schiff base, L



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	428.21	2.8946	0.0152	447.5	391.56	85.9658	0.0704
2	534.3	2.6566	0.2886	592.17	448.46	223.0102	2.8604
3	630.74	2.9071	0.0927	697.29	593.13	159.1817	0.6937
4	727.19	3.022	0.0644	773.48	698.25	113.9038	0.3936
5	830.38	2.6069	0.6614	895.96	774.45	185.8089	5.3778
6	1022.31	2.7187	0.5011	1070.53	896.93	262.6003	4.8251
7	1160.22	2.6213	0.2405	1195.91	1071.49	193.3251	2.8175
8	1242.2	2.4562	0.4461	1343.46	1196.87	227.4826	3.9938
9	1498.74	2.3836	0.5371	1552.75	1344.43	325.13	8.5235
10	1623.15	2.2892	0.6034	1763.96	1553.71	329.4219	7.3716
11	1788.07	3.0692	0.0007	1801.57	1764.93	55.4465	0.0018
12	1911.52	2.9747	0.0109	1925.02	1802.54	186.2028	0.1313
13	2060.04	2.8608	0.0243	2088.98	1925.99	250.2544	0.2268
14	2274.15	2.7226	0.0853	2333.94	2089.94	379.3165	1.4488
15	2942.51	2.0293	0.1538	2994.59	2334.91	1062.0609	2.6432
16	3406.4	0.9232	1.1031	3718.88	2995.55	1318.1174	94.9461
17	3751.67	1.9384	0.0163	3800.86	3719.85	138.5585	0.1523
18	3878.01	1.9261	0.0021	3881.87	3801.82	136.9834	0.0569
19	3890.55	1.9259	0.0001	3898.27	3882.84	26.4696	0.0003

Fig 1: FTIR result for L



Co

FTIR ANALYSIS RESULT
NATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA
SHIMADZU
FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

NAME: SAIDU ABDULLAHI, SAMPLE: Co L1 (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	401.21	2.207	0.5522	435.93	349.13	139.122	4.6249
2	536.23	1.878	0.4072	596.02	436.89	266.8	5.9548
3	645.21	2.1314	0.0769	681.86	596.99	141.15	0.7034
4	732.97	2.0755	0.0789	765.77	682.82	138.8443	0.665
5	830.38	1.4647	0.744	896.93	766.73	225.8521	10.2573
6	1020.38	1.5332	0.533	1073.42	897.89	302.7777	9.0619
7	1169.87	1.496	0.054	1181.44	1074.39	190.3714	1.5954
8	1241.23	1.1656	0.5382	1344.43	1182.4	294.7048	10.3928
9	1494.88	1.2928	0.5063	1549.86	1345.39	366.1246	13.0239
10	1610.61	1.2317	0.5634	1717.67	1550.82	300.8339	10.8692
11	1907.66	1.8	0.0294	1940.45	1718.63	382.8436	0.4342
12	2052.33	1.7156	0.0439	2105.37	1941.42	287.9746	0.7993
13	2362.88	1.5659	0.0525	2417.85	2106.34	556.0831	1.9606
14	2557.69	1.5134	0.0117	2578.91	2418.82	289.8739	0.3238
15	2939.61	1.0851	0.1851	3007.12	2579.88	801.911	7.1696
16	3406.4	0.6327	0.5589	3719.85	3008.09	1443.8079	75.3127
17	3756.49	1.1586	0.0114	3808.57	3720.81	169.7068	0.1924

Fe

FTIR ANALYSIS RESULT
NATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA
SHIMADZU
FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

NAME: SAIDU ABDULLAHI, SAMPLE: Fe L1 (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	473.54	2.4504	0.0456	489.94	365.52	198.3882	1.1971
2	533.34	2.3683	0.1669	589.27	490.9	158.2375	1.4055
3	644.25	2.49	0.1686	771.55	590.24	288.1953	2.9883
4	832.31	2.1698	0.5933	896.93	772.52	199.7135	5.8262
5	1022.31	2.2076	0.4403	1070.53	897.89	275.8938	5.0544
6	1163.11	2.1209	0.1806	1194.94	1071.49	202.8088	2.5654
7	1243.16	1.9281	0.4061	1342.5	1195.91	242.2086	4.6893
8	1498.74	1.8593	0.4601	1552.75	1343.46	348.8398	10.0943
9	1620.26	1.8068	0.4848	1748.53	1553.71	325.5513	7.3515
10	1907.66	2.3413	0.008	1922.13	1749.49	279.7865	0.0806
11	2061.01	2.2455	0.0191	2088.98	1923.09	272.059	0.2321
12	2278.01	2.1186	0.0447	2324.3	2089.94	389.5714	0.9026
13	2390.85	2.0889	0.0177	2416.89	2325.26	153.5602	0.1763
14	2943.47	1.5399	0.101	2989.76	2417.85	988.7926	1.6312
15	3405.44	0.7968	0.7775	3729.49	2990.73	1418.0152	86.6602
16	3754.56	1.5497	0.0079	3798.93	3730.45	123.8183	0.0804
17	3938.77	1.5239	0.0093	3969.64	3799.89	307.8458	0.4716

Mn

FTIR ANALYSIS RESULT
NATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA
SHIMADZU
FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

NAME: SAIDU ABDULLAHI, SAMPLE: Mn L1 (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	537.19	2.8174	0.3871	590.24	391.56	301.7787	7.9322
2	632.67	2.9837	0.0886	703.08	591.2	169.8602	0.6955
3	725.26	3.0812	0.0402	774.45	704.04	106.059	0.2579
4	831.35	2.7303	0.5564	895.96	775.41	183.1342	4.3995
5	1023.27	2.8076	0.4098	1069.56	896.93	260.2144	3.7845
6	1160.22	2.6811	0.2241	1195.91	1070.53	193.8962	2.5379
7	1241.23	2.5538	0.3873	1343.46	1196.87	226.0047	3.2334
8	1498.74	2.4799	0.4782	1552.75	1344.43	322.8501	7.0516
9	1623.15	2.4231	0.5042	1753.35	1553.71	311.2349	6.0475
10	1905.73	2.9673	0.0083	1919.24	1754.32	250.5929	0.064
11	2065.83	2.8551	0.0079	2076.44	1920.2	239.9818	0.1122
12	2285.72	2.7188	0.0164	2307.9	2077.4	358.4833	0.2309
13	2377.34	2.6534	0.04	2420.74	2308.87	175.8445	0.3342
14	2940.58	2.1065	0.1413	2994.59	2421.71	923.501	2.1924
15	3406.4	1.0921	1.0025	3727.56	2995.55	1310.1147	82.621
16	3759.39	2.003	0.0112	3802.79	3728.53	126.0115	0.0848
17	3914.66	1.9744	0.0046	3925.27	3803.75	206.691	0.1812

Ni

FTIR ANALYSIS RESULT
ATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA
SHIMADZU
FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

NAME: SAIDU ABDULLAHI, SAMPLE: Ni L1 (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	537.19	2.9437	0.5181	590.24	349.13	357.8401	13.9245
2	637.49	3.0972	0.1019	695.36	591.2	156.4704	0.7461
3	732.01	3.1556	0.0644	771.55	696.33	112.5973	0.3594
4	831.35	2.6699	0.6376	895	772.52	186.4436	5.1279
5	1022.31	2.6898	0.4638	1070.53	895.96	264.9756	4.4444
6	1162.15	2.5983	0.1804	1193.01	1071.49	189.5292	2.1382
7	1241.23	2.3566	0.4591	1341.54	1193.98	231.5014	4.2732
8	1430.26	2.5782	0.0543	1439.91	1342.5	151.3101	0.6878
9	1498.74	2.3058	0.3273	1552.75	1440.87	179.7543	2.9955
10	1620.26	2.2632	0.4766	1745.64	1553.71	304.9106	5.8886
11	1794.82	2.8436	0.0001	1795.79	1746.6	76.0336	0.0027
12	2280.9	2.491	0.0374	2318.51	1796.75	822.515	1.4713
13	2389.88	2.433	0.0252	2419.78	2319.48	161.4059	0.2241
14	2943.47	1.8692	0.0957	2988.8	2420.74	941.332	1.2214
15	3408.33	1.0212	0.8174	3715.99	2989.76	1330.1376	71.4506
16	3754.56	1.7597	0.0214	3801.82	3716.95	148.6769	0.2226
17	3910.8	1.738	0.003	3917.56	3802.79	201.4508	0.1797
18	3957.1	1.7353	0.0063	4000.5	3918.52	144.2703	0.0721

Fig 2: FTIR results for the Schiff base metal complexes

DISCUSSIONS

The interaction between 4-methoxybenzaldehyde with *p*-anisidine gave a grey coloured crystals of Schiff base L, called (E)-4-methoxy-N-(4-methoxybenzylidene) aniline. The percentage yield of the Schiff base ligand was 84.64% and with a melting point of 153-174ºC. The reactions of the Schiff base L. with the respective metal (II) chlorides ($NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $FeCl_2.4H_2O$ or $MnCl_2.4H_2O$) produced complexes that are variously coloured with percentage yield in the range 83-90% . The ligand and its complexes have sharp melting points, an indication of purity for the substances prepared. The complexes are all anhydrous and air stable. The Schiff base and their complexes were found to be soluble in most solvents (Table 6). The molar conductance (Table 3) of the complexes in dimethylsulphoxide was in the range of 77.58-85.10 $\Omega^{-1}mol^{-1}cm^2$ for L, which suggests the presence of anion outside the coordination sphere. These values are in good agreement with those reported earlier [11,12, 13, 14, 15]. The magnetic moment values of the complexes obtained (Table 4) was in the range of 4.62-5.34 B.M and was an indication of paramagnetic nature of the complexes due to the presence of unpaired electrons in the partially filled d-orbitals. The positive X_m value confirmed that substances have unpaired electrons; this is in agreement with what has been reported earlier [16]. Gravimetric analysis data (Table 2) for the complexes obtained showed that the complexes analyzed as ML2 and the results obtained were in good agreement with the calculated values. A plot of absorbance (*y axis*) versus the mole fraction (*x axis*) of the ligand revealed a stoichiometric values of 1:2 metal-ligand ratio.

Infrared: Table 2 revealed the infrared spectra of the ligand which showed a characteristic band at 1623-1627 cm^{-1} which is attributable to υ C=N band. This band shifted to a lower range of frequencies 1610-1623cm^{-1}in the complexes ML; this indicates involvement of theazomethine nitrogen in bonding, the result bands are similar to the values reported by [17, 18]. The band at 2942cm^{-1} in the ligand, which was present in the spectra of its corresponding complexes was assigned to υ O-CH_3andit indicated the non-involvement of the methyl group in complexation as also reported by [19]. The coordination through nitrogen of azomethine and oxygen of υ O-CH_3 group of the ligand with its complexes are further evidenced by the appearance in the complexes of new but low frequency non-ligand bands around 632-645cm^{-1} and 533-537cm^{-1} assigned to υ M-N and υ M-O respectively. These bands were absent in the ligand. The shifting of the band at 1623 cm^{-1} to lower values in all the complexes, low frequency bands (around 632-645cm^{-1}) and the vibration centered around 2942cm^{-1} υ O-CH_3revealed that complexation has taken place and that azomethine and oxygen of the methoxygroups were involved in coordination to the metal ion, this implied that the ligand L, was tridented.

The antimicrobial analysis of the compounds obtained (Tables 7a and 7b), revealed that the metal complexes have higher antibacterial activity than the free ligand. This suggests that chelation increases the antibacterial activity of the compounds as reported by [17, 18, 19].

CONCLUSION

(E)-4-methoxy-N-(4-methoxybenzylidene) aniline and its transition metal complexes have been synthesized in 2:1 molar ratio of ligand to metal ion. The complexes are all air stable and are anhydrous. Infrared studies have shown that L coordinated as a tridentate ligand. Job's method of mole ratio determination for the complexes revealed the stoichiometric compositions for the complexes as 1:2 molar ratio (metal:ligand). Magnetic susceptibility studies showed the metals to be paramagnetic in nature for all the complexes. Antibacterial studies have indicated thatthe complexes showed higher activities than the free ligand. The results of these investigations support the suggested structure of the metal complexes.

ACKNOWLEDGEMENTS

The authors acknowledge the invaluable efforts and assistance of the Laboratory Technologists in the Departments of Pure/Industrial Chemistry and Microbiology, Bayero University respectively.

REFERENCES

1. AOCS Official Method Cd 18-90. American Oil Chemists' Societyhttps://aocs.personifycloud.com/PersonifyEBusiness/Default.aspx?Ta ID=258.
2. Abbas, N. A., Salih H. K, and Waleed, A. J. (2013).Synthesis and study of Fe(III), Co(II), Ni(II) and Cu(II) complexes of new Schiff's base ligand derived from 4-aminoantipyrine, *Journal of Applicable Chemistry,* 2(3), 438-446.
3. Anita, S, and Manish, S. (2013).Synthesis and characterization of some transitionmetalcomplexes derived from bi-dentate Schiff base ligand,*IOSR Journal of AppliedChemistry (IOSR-JAC),* 3(5), 62-66.
4. Barboiu C.T., Luca M., Pop C., Brewster E., Dinculescu M.E. (1996), Synthesis of mono and bis pyridinium salt derivatives of 2-amino-5-(2-aminoethyl)- and 2-amino-5-(3aminopropyl)- 1,3,4-thiadiazole and their interaction with Isozyme II. *European Journal of Medicinal Chemistry.* 31, 597.
5. Daniel C. Harris, (2007). Quantitative Chemical Analysis - Seventh Edition, W. H.Freeman and Company New York Pp. 629-637 ISBN: 0-7167-7041-5.
6. Gaur, S. (2003). Physico-chemical and Biological properties of Mn(II), Co(II), Ni(II) and Cu(II)Chelates of Schiff bases. *Asian Journal of Chemistry*, 15(1), 250 -254.
7. Geary, W. J. (1971). The use of conductivity measurements in organic solvents for the characterization of coordination compounds, *Coord. Chemistry Review.* 7, 8 -122.
8. Vogel, A. I. (1989). Vogel's textbook of quantitative chemical analysis, 5th Ed. Pp.454, 457, 460,462. Longman Group UK Limited, Longman House, Burnt Mill, Harlow, Essex CM20 2JE, England. ISBN 0-582-44693-7
9. Genin, M J., Biles, C.., Keiser, B.J., Poppe, S.M., Swaney, S.M., Tarapley, W.G., Romeso, D.L., Yage, Y. (2000). Novel 1,5-

diphenylpyrazole non-nucleoside HIV-1 Reverse Transcriptase Inhibitors with Enhanced Activity versus the Delavirdine – Resistant P236L Mutant: Lead Identification and SAR of 3- and 4- substituted Derivatives. *Journal of Medicinal Chemistry,* 43(5), 1034- 1040.

10. Hasan, H. Monfared., Omid, P, and Christoph, J. (2007): Synthesis and Spectral characterization of Hydrazone Schiff bases derived from 2,4-dinitrophenylhydrazine; Crystal structure of Salicylaldehyde-2,4-dinitrophenylhydrazone. *Z Naturforsch,* 62b: 717-72
11. Keypour H., Rezaeivala M., Valencia L., Perez- Lourido P., Raza Khavasi H. (2009). Synthesisand Characterization of some new Co(II) and Cd(II) macroacylic Schiff-base complexes containing piperazine moiety, *Polyhedron,* 28(17), 3755.
12. Kolawole, G. A., N. P. Ndahi. (2004). Cobalt(III) complexes of dimethylglyoxime with no directcobalt-carbon as possible non organometallic models of vitamin B12. *Synth. React. Met.Org.Chem,* 34(9), 1563-1580.
13. Lotf, A. S., Ali, A., Sohrab, E., Ghasem, K., Shahriar, G., Roya, K. (2008). Preparation of Zn(II) and Cd(II) complexes of the Tetradentate Schiff base ligand2-[(E)-2-(2pyridine-2yl)ethylthio)ethylimino)methyl)-4-bromophenol(PytBrSalH), *Molecules,* 13, 804-811.
14. Nakamato, K. (1971). Infrared spectra of inorganic and coordination compounds, John Wiley and Sons, New York. Pp.125-130
15. Ndahi, N. P., Nasiru, Y. P., Sandabe, U. K. (2012). Synthesis, characterization and antibacterial studies of some Schiff base complexes of Co(II), Ni(II) and Zn(II). *Asian Journal of Biochemical and Pharmaceutical Research,* 1(2), 2231-2560.
16. Reddy, V., Patil, N., Angadi, S. D. (2008). Synthesis, Characterization and AntimicrobialActivity of Cu(II), Co(II) and Ni(II) Complexes with O,N, and S Donor Ligands, *E-J. Chem,* 5(3), 577-583
17. Yousif, Emad., Ahmed, Majeed., Khulood, Al-Sammarrae., Nadia, Salih., Jumat, Salimon., Bashar, Abdullah. (2013). Metal complexes of Schiff base: Preparation, Characterization and Antibacterial activity. *Arabian Journal of Chemistry,*http://dx.doi.org/10.1016/j.arabjc.2013.06.006.
18. Zahid, H. C., Asifa, M., Claudiu, T. S. (2009). Transition metal ion complexes of Schiff-bases,synthesis, characterization and antibacterial properties. *Metal Based Drugs,* 8(3), 137- 143.
19. Zahid, H. C., Maimoon, F. J. (2000). Synthesis, characterization and biological evaluation of Co(II), Ni(II) and Zn(II) complexes with

Cephradine, *Metal Based Drugs,* 7(5), 265-269