

Synthesis, Characterization and Anti-Microbial Studies of Metal(II) complexes with 4-methoxybenzaldehyde with *p*-anisidine

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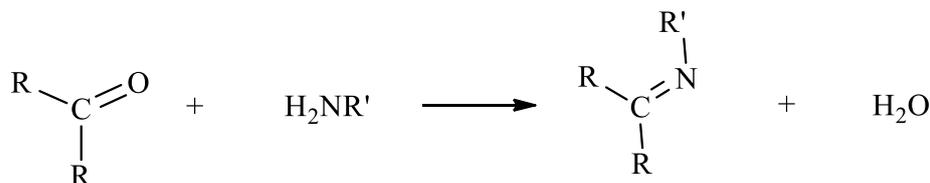
Citation: Sayeed, A., Na'aliya, J., Ethan, W. (2022) Synthesis, Characterization and Anti-Microbial Studies of Metal(II) complexes with 4-methoxybenzaldehyde with *p*-anisidine, Global Journal of Pure and Applied Chemistry Research, Vol.10, No.1, pp.23-38,

ABSTRACT: *Some divalent transition metal complexes were synthesized by the reaction of the chlorides of Co(II), Fe(II), Mn(II) and Ni(II) with Schiff bases derived from the reaction of 4-methoxybenzaldehyde with p-anisidine in methanolic solution. The Schiff base [L] was obtained as grey colored crystals with a melting point of 153°C. The metal(II) complexes [ML] obtained were all colored and decomposed at the range of 171-177 °C. Molar conductivity measurements for the complexes carried out using DMSO were found to be at the range of 1.19-16.07Ω⁻¹mol⁻¹cm². The small values could be an indication for non-electrolytic nature of the complexes. From the values of the magnetic moment (4.40–5.85 B.M), all the complexes were found to be paramagnetic and soluble in most common solvents. The infra-red spectral analysis indicates complexation has taken place due to metal-nitrogen bands at the range, 632–645cm⁻¹ for [ML]. The metal-ligands ratio in all the complexes was 1:2 as obtained from the Job's method of continuous variation. The percentage composition of the metals and their corresponding ligands were found gravimetrically and the results obtained were in good agreement with the calculated values. The ligands and their corresponding complexes were screened in-vitro for their antimicrobial activity against Escherichia coli, Aspergillus fumigatus, Salmonella typhi, Staphylococcus aureus, Aspergillus flavus and Mucor species using the paper-discs diffusion method. Inhibition properties of the compounds showed that the complexes have higher antimicrobial activities than the ligands which could be attributed to chelation.*

KEYWORDS: Imine, ligands, complexes, paramagnetic, antimicrobial activity and chelation.

INTRODUCTION

Schiff bases, imines or azomethines named after Hugo Schiff (1834-1915) are the nitrogen analogs of ketones and aldehydes but imine is the preferred name and it is so commonly used. These compounds can be prepared by condensation of primary amines with ketones or aldehydes. For a favorable equilibrium constant, the reaction is usually driven forward by removal of water.



Scheme 1. Equation of reactions

R here stands for a phenyl or alkyl group which makes the Schiff base a stable imine. It is able to coordinate metal ion through the imine nitrogen and another group, usually linked to the aldehyde. Mechanistically, the formation of an imine involves two steps; first the amine nitrogen acts as a nucleophile, attacking the carbonyl atom; the nitrogen is deprotonated, and the electron from this N-H bond “push” the oxygen off from the carbon, leaving behind a C=N double bond (an imine) and a displaced water molecule. The common Schiff bases are crystalline solids which are feebly basic but at least some form insoluble salts with strong acids (Mahmud, 2010), in complete derivatives the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antimicrobial activity, antifungal, anticancer and diuretic activities (Barboiu *et al.*, 1996). Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities. Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Keypour *et al.*, 2009). A considerable number of Schiff base complexes have potential biological interest, being used as more or less successful models of biological compounds. Not only have they played a seminal role in the development of modern coordination chemistry, they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials. Their use in birth control and as an O₂ detector is also outlined (Anant and Devjani, 2011). Schiff base chelates are also used in quantitative analysis as an analytical chemical reagent and as separation reagents (Bader, 2010) and also in synthetic applications in the field of organic and inorganic chemistry (Pallavi *et al.*, 2014).

LITERATURE REVIEW

Jain and Valecha in 2015 reported the Synthesis and characterization of Schiff base derived from 4-benzoyl-3-methyl-1-phenylpyrazol-5-one and *p*-anisidine respectively. The Schiff base slightly inhibited only gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*), while the Ni(II) and Co(II) complexes also inhibited the growth of only gram positive bacteria and was reported as a highly active complex. Mn(II) complex inhibited only a single gram positive bacteria (*S. aureus*). The least activity was shown by Cr(III) complex as no bacteria was inhibited. Feroza *et al.*, (2012) reported the Synthesis, spectroscopic characterization and antibacterial activities of three Schiff bases derived from dehydroacetic acid with various substituted anilines. Their antibacterial activities were investigated against four bacteria, two gram positive (*Staphylococcus aureus*, *Bacillus subtilis*), and two gram negative bacteria strains (*Escherichia coli* and *Pseudomonas aureginosa* by the agar well diffusion method. The

Schiff base showed better antibacterial activity when compared with other Schiff bases against the studied microbes. Conclusively, these newly reported Schiff bases have potential antibacterial activities against four strains of bacteria like *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aureginosa*. Dioxouranium(VI) complexes of some monovalent bidented Schiff base ligands derived from aniline were reported by Didarul *et al.*, in 2011. The results suggested that the Schiff base is a monovalent anion with bidented ON donor atoms of the phenolic oxygen and the azomethine nitrogen atoms. The formulae were found to be UO_2L_2 for the 1:2 non-electrolytic complexes, and six coordinate structures were proposed for it. The temperature effect on solution stability constants of metal complexes with Schiff bases derived from 5-aldehydosalicylic acid-aniline and its related compounds were reported by Basavaraj *et al.*, (2011). The solution stability constants of their complexes with bivalent metal ions Cu(II), Zn(II), Ni(II), Co(II), Cd(II) and Mg(II) was determined at four temperatures in 50% water-ethanol mixture at an ionic strength of 0.1M($NaClO_4$). The order of solution stability constants was found to be $Zn < Cu > Ni > Co = Cd > Mg$ which was in agreement with Irving-Williams order. The values of ΔG_o , ΔH_o , ΔS_o was calculated for the various complex equilibrium and copper chelates were found to be more stable than Zn and Ni chelates due difference in their configurations. Cu(II) formed square planar complex while Zn(II), Ni(II) formed a tetrahedral or octahedral complexes. The logK value for Zn chelate was found to be higher as compared to that of Ni chelate in all the reagents used for the investigation. In 2011, Aliyu and Bilyamin reported Studies on bis(*para*-anisidineacetylacetonato)nickel(II) complex. The molar conductance of the bis(*para*-anisidineacetylacetonato)nickel(II) complex compound determined was $4.70 \Omega^{-1}cm^2 mol^{-1}$, suggesting that the complex was non-electrolyte. The average number of *para*-anisidine ligand coordinated to Ni(II) ion determined using potentiometer was 2, suggesting a four coordinated compound. Manimekalai (2011) reported transition metal complexes of phenylacetates with neutral hydrazine as a ligand, where some hydrazine carboxylates of the type $Co(PhAc)_2(N_2H_4)_2$, where M = Co, Ni, Cd and Mn, $M(di-PhAc)_2.5N_2H_4$, M = Co, Ni and Cd, $M(2,4 di-ClPh.Ac)_2.5N_2H_2.H_2O$ where M = Co, Ni and Cd, have been prepared and studied. The electronic spectra suggested an octahedral geometry for the metal complexes. The IR absorption bands of N-N stretching in the range $958-957cm^{-1}$ unambiguously prove the bidented bridging nature of the N_2H_4 ligand. All the prepared complexes underwent two, three or multi step decomposition and the final products were found to be the respective metal oxide, metal carbonate, metal of mixture of metal oxide and metal carbonate or metal as indicated by thermal analysis. In order to know the isomorphous nature among the complexes, the X-ray patterns were compared.

MATERIALS AND METHODS

Reagents

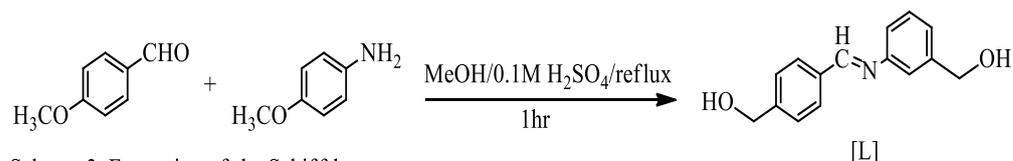
Reagents of analytical grade purity and distilled water were used without further purification. All glassware used were well washed with detergent, concentrated nitric acid (0.1M) and rinsed with distilled water and dried in an oven at $110^\circ C$.

Instruments

All weighing were carried out on an electric metlar balance model H3OAR, melting point and decomposition temperatures were measured using Stuart SMP-10 (Digital) melting point apparatus and were uncorrected. Molar conductance measurements were determined using Jenway Conductivity meter 4010 model. IR spectral were recorded using FTIR 8400S (Fourier Transformed Infrared Shimadzu Spectrophotometer) in KBr at the range of 400-4000 cm^{-1} and 300-1000 cm^{-1} respectively. The antimicrobial and antifungal evaluations were performed at the Department of Microbiology, Bayero University, Kano.

Synthesis of the Schiff base

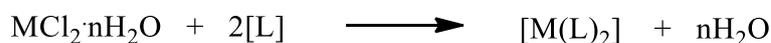
0.1M H_2SO_4 was added to an equimolar amount of 4-methoxybenzaldehyde and *p*-anisidine in a 50 cm^3 methanolic solution (1:1) molar ratio to give [L]. The mixture was refluxed for one hour after which it was cooled to room temperature. The product formed was concentrated, filtered, washed with 3 x 15 cm^3 portions of ethanol and dried over anhydrous P_2O_5 in a desiccator (Ndahi *et al.*, 2012).



Scheme 3. Formation of the Schiff base

Synthesis of the Metal(II) Complexes

3mmol of the corresponding metal salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 25 cm^3 methanol) was added separately to a solution of the Schiff base ligand [L] in 10 cm^3 methanol, with constant stirring. The mixture was refluxed for 2 hours using hot plate magnetic stirrer, after which it was allowed to cool at room temperature and the product formed was concentrated, filtered and washed with 3x10 cm^3 portions of ethanol and stored in a desiccator containing anhydrous P_2O_5 (Ndahi *et al.*, 2012). The general equations leading to the formation of the complexes is given below:



where M = Mn(II), Fe(II), Co(II) or Ni(II); [L] = Schiff base derived from 4-methoxybenzaldehyde and *p*-anisidine.

Antibacterial Activity

Potato dextrose (pH of 5.5 at 25°C) and Nutrient agar were prepared separately and autoclaved before used for antibacterial activities. The ligands and complexes were dissolved separately in DMSO at different concentrations per disc, they were then placed separately on the surface of the culture using a sterile wire loop and incubated at 37°C for 24hrs. The diameter of the zones of inhibition surrounding the discs was taken as the measure of inhibitory power of the sample against a particular test

organism. The in-vitro antibacterial activity was carried out by paper disc diffusion method

RESULTS

Table 1: Physical properties of the ligand and the complexes

Compounds	Formular	Formular wt (g)	Colour	Yield	M.pt/Decomp. Tempt (°C)
[L]	C ₁₅ H ₁₅ NO ₂	241.28	Grey	84.64	153
[CoL]	[Co(L) ₂]	541.50	Yellow	84.94	171d
[FeL]	[Fe(L) ₂]	538.41	Brown	83.42	176d
[MnL]	[Mn(L) ₂]	537.51	Yellow	90.87	174d
[NiL]	[Ni(L) ₂]	541.26	Green	89.20	177d

Key: [L] = C₁₅H₁₅NO₂

Table 2: Infrared spectral data of the ligands and complexes

Compounds	ν C=N	ν M-N	ν M-O	ν O-H
[L]	1623			3719
[CoL]	1610	645	536	
[FeL]	1620	644	533	
[MnL]	1623	632	537	
[NiL]	1620	637	537	

Key: [L] = C₁₅H₁₅NO₂

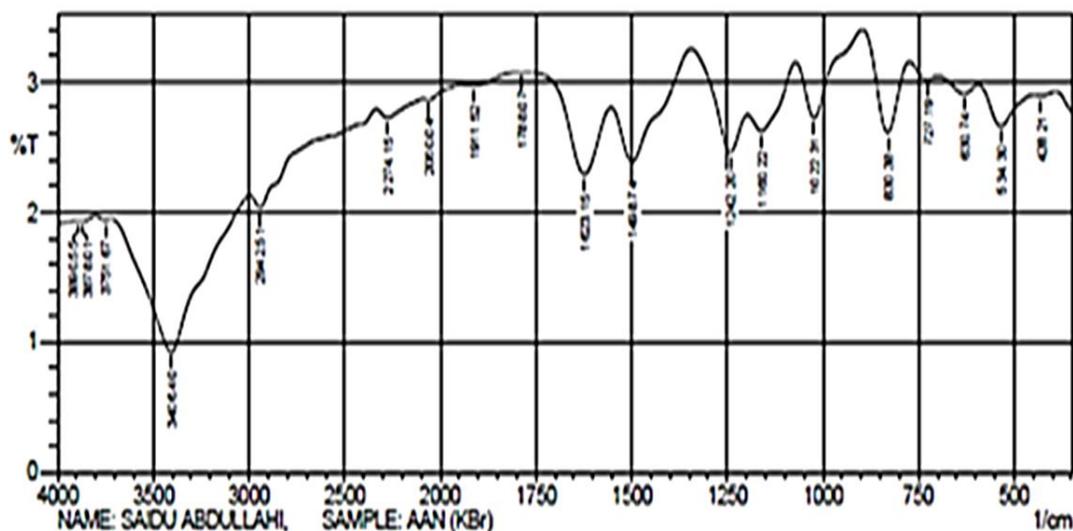
Schiff base [L]

FTIR ANALYSIS RESULT

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FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



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	1768.07	3.0892	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	3800.66	3719.85	138.5585	0.1523
18	3878.01	1.9261	0.0021	3881.87	3801.82	136.9834	0.0549
19	3890.55	1.9259	0.0001	3898.27	3882.84	26.4696	0.0003

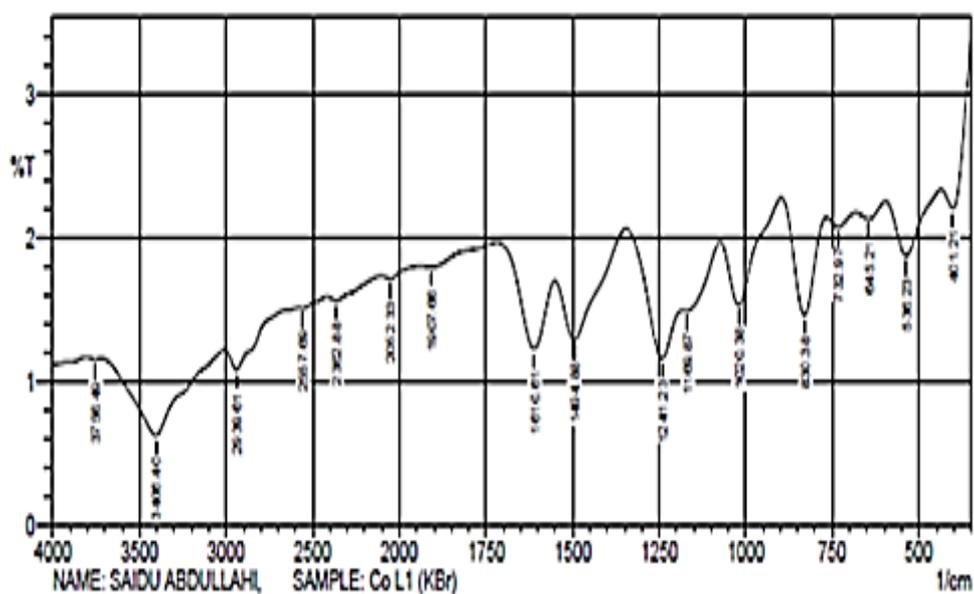
[Co(L)₂]

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FTIR-3400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



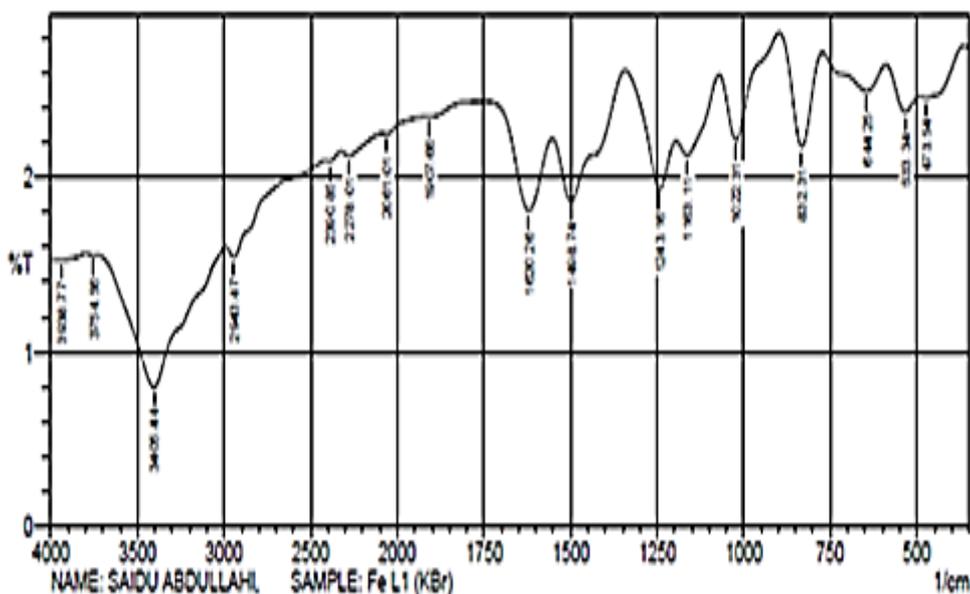
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	401.21	2.207	0.5522	435.93	349.13	139.122	4.6249
2	536.23	1.878	0.4072	596.02	436.89	266.8	5.9548
3	645.21	2.1314	0.0769	681.86	596.99	141.15	0.7034
4	732.97	2.0755	0.0789	765.77	682.82	138.8443	0.665
5	830.38	1.4647	0.744	896.93	766.73	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(L)₂]

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FTIR-8400S FOURIER TRANSFORM
 INFRARED SPECTROPHOTOMETER



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

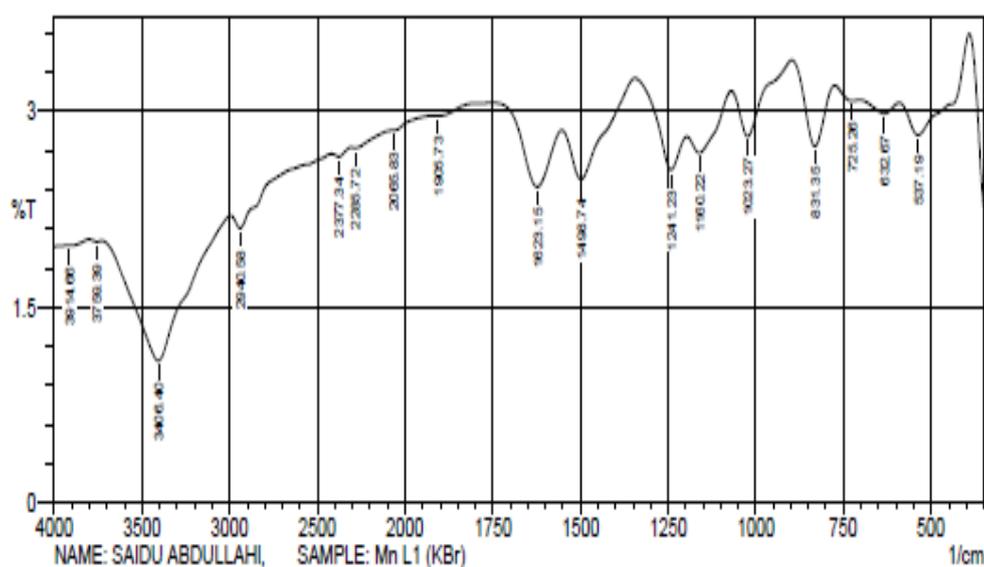


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FTIR-8400S FOURIER TRANSFORM
INFRARED SPECTROPHOTOMETER



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	0.5554	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

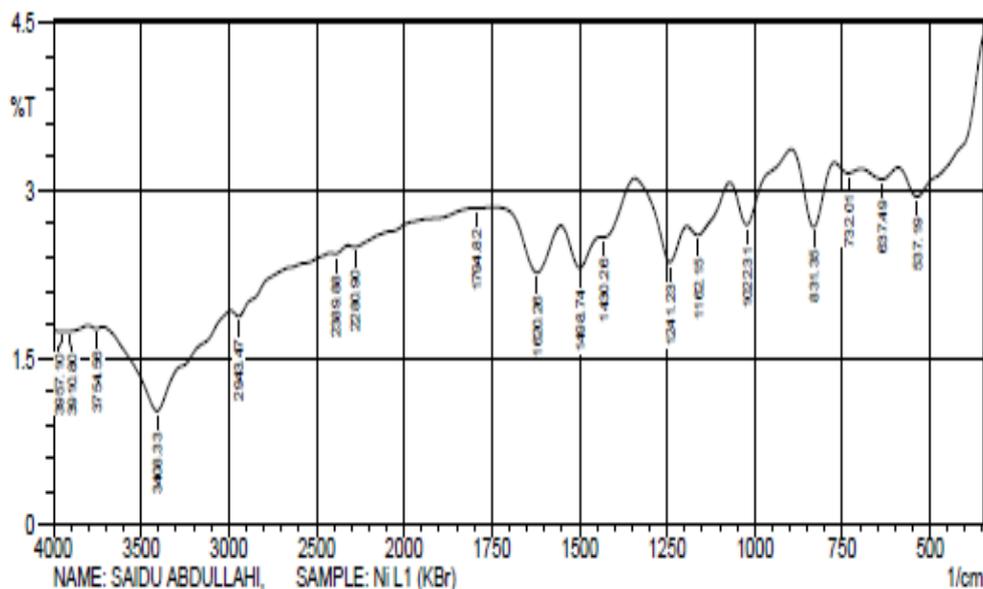


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FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



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

Table 3: Molar conductivity of the Schiff base complexes

Compound	Concentration, C (mol)	Specific conductance (S)	Molar conductivity: $[\lambda = \frac{S}{C}] \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
[CoL]	1×10^{-3}	77.58×10^{-6}	77.58
[FeL]	1×10^{-3}	85.10×10^{-6}	85.10
[MnL]	1×10^{-3}	79.95×10^{-6}	79.95
[NiL]	1×10^{-3}	80.55×10^{-6}	80.55

Key: [L] = C₁₅H₁₅NO₂ λ = Molar conductance C = Molar concentration

S = specific conductance

Table 4: Solubility of the compound in water and some common organic solvents

Solvents	[L]	[CoL]	[FeL]	[MnL]	[NiL]
Acetone	S	S	S	S	S
CCl ₄	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
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] = C₁₅H₁₅NO₂

Table 5: MAGNETIC SUSCEPTIBILITY OF THE COMPLEXES

Compounds	Gram susc, X _g ergc ⁻² g ⁻¹	Molar susc, X _m	Effective mag. moment (μ _{eff})	Unpaired B.M electrons	Geometry
[CoL]	1.62 x 10 ⁻⁵	8.75 x 10 ⁻³	4.62	7	Octahedral
[FeL]	2.04 x 10 ⁻⁵	1.10 x 10 ⁻²	5.17	6	Octahedral
[MnL]	1.67 x 10 ⁻⁵	8.96 x 10 ⁻³	4.68	5	Octahedral
[NiL]	2.18 x 10 ⁻⁵	1.20 x 10 ⁻²	5.34	8	Octahedral

Key: [L] = C₁₅H₁₅NO₂

Table 6: ANTIBACTERIAL ACTIVITIES OF THE COMPOUNDS

Compound	Organism	Concentration (μg)/Zone of inhibition (mm)					
		5000	4000	3000	2000	1000	Control (mm)
[L]	<i>S. aureus</i>	18	14	12	07	04	30 (Ampiclox)
[L]	<i>E. coli</i>	24	16	10	10	08	32 (Ampiclox)
[L]	<i>S. typhi</i>	20	18	14	06	04	30 (Ampiclox)
[L]	<i>A. fumigatus</i>	22	20	16	10	07	27(Ciprofoxacin)
[L]	<i>A. flavus</i>	26	26	23	20	15	30 (Ciprofoxacin)
[L]	<i>Mucor. S</i>	24	22	18	20	14	33 (Ciprofoxacin)
[CoL]	<i>S. aureus</i>	24	19	NZI	14	10	32 (Ampiclox)
[CoL]	<i>E. coli</i>	26	19	16	14	NZI	34 (Ampiclox)
[CoL]	<i>S. typhi</i>	22	18	14	NZI	10	34 (Ampiclox)
[CoL]	<i>A. fumigatus</i>	28	20	17	12	08	30 (Ciprofoxacin)
[CoL]	<i>A. flavus</i>	26	20	16	12	NZI	32 (Ciprofoxacin)
[CoL]	<i>Mucor. S</i>	28	18	14	10	NZI	33 (Ciprofoxacin)
[FeL]	<i>S. aureus</i>	19	12	07	04	NZI	28 (Ampiclox)
[FeL]	<i>E. coli</i>	16	12	12	10	06	32 (Ampiclox)
[FeL]	<i>S. typhi</i>	19	13	11	07	04	30 (Ampiclox)
[FeL]	<i>A. fumigatus</i>	16	12	NZI	NZI	02	34 (Ciprofoxacin)
[FeL]	<i>A. flavus</i>	20	14	10	06	NZI	30 (Ciprofoxacin)

[MnL]	<i>S. aureus</i>	26	16	12	07	03	28 (Ampiclox)
[MnL]	<i>E. coli</i>	18	12	07	04	NZI	31 (Ampiclox)
[MnL]	<i>S. typhi</i>	24	17	14	10	06	34 (Ampiclox)
[MnL]	<i>A. fumigatus</i>	22	16	14	08	04	30 (Ciprofoxacin)
[MnL]	<i>A. flavus</i>	18	12	10	06	02	32 (Ciprofoxacin)
[MnL]	<i>Mucor. S</i>	22	10	03	NZI	NZI	30 (Ciprofoxacin)
[NiL]	<i>S. aureus</i>	28	22	16	10	06	34 (Ampiclox)

Key: [L = C₁₅H₁₅NO₂

NZI = No zone of inhibition

Ampiclox = (500mg per disc)

Ofloxacin = (500mg per disc)

Table 4.6b: cont

[NiL]	<i>E. coli</i>	22	14	NZI	NZI	02	31 (Ampiclox)
[NiL]	<i>S. typhi</i>	26	18	16	08	NZI	34 (Ampiclox)
[NiL]	<i>A. fumigatus</i>	24	17	13	10	06	30 (Ciprofoxacin)
[NiL]	<i>A. flavus</i>	26	22	14	07	02	32 (Ciprofoxacin)
[NiL]	<i>Mucor. S</i>	NZI	NZI	NZI	NZI	NZI	33 (Ciprofoxacin)
[MnL]	<i>S. aureus</i>	26	16	12	07	03	28 (Ampiclox)
[MnL]	<i>E. coli</i>	18	12	07	04	NZI	31 (Ampiclox)
[MnL]	<i>S. typhi</i>	24	17	14	10	06	34 (Ampiclox)
[MnL]	<i>A. fumigatus</i>	22	16	14	08	04	30 (Ciprofoxacin)
[MnL]	<i>A. flavus</i>	18	12	10	06	02	32 (Ciprofoxacin)
[MnL]	<i>Mucor. S</i>	22	10	03	NZI	NZI	30 (Ciprofoxacin)
[NiL]	<i>S. aureus</i>	28	22	16	10	06	34 (Ampiclox)
[NiL]	<i>E. coli</i>	22	14	NZI	NZI	02	31 (Ampiclox)
[NiL]	<i>S. typhi</i>	26	18	16	08	NZI	34 (Ampiclox)
[NiL]	<i>A. fumigatus</i>	24	17	13	10	06	30 (Ciprofoxacin)
[NiL]	<i>A. flavus</i>	26	22	14	07	02	32 (Ciprofoxacin)
[NiL]	<i>Mucor. S</i>	NZI	NZI	NZI	NZI	NZI	33 (Ciprofoxacin)

Key: [L = C₁₅H₁₅NO₂

NZI = No zone of inhibition

Ampiclox = (500mg per disc)

Ofloxacin = (500mg per disc)

DISCUSSION

The interaction between 4-methoxybenzaldehyde with *p*-anisidine gave grey colored crystals of Schiff base [L]. The percentage yield of the Schiff base [L] was 84.64% with melting point at 153°C. The reaction of the Schiff base, [L] with the metal(II) chlorides (NiCl₂.6H₂O, CoCl₂.6H₂O, FeCl₂.4H₂O or MnCl₂.4H₂O) produced complexes that are variously colored with percent yields in the range 84-90%. The ligand [L] have sharp melting point while its complexes decomposed thermally. The sharp melting point observed in the ligand was an indication of purity for the substance prepared. The high values of the decomposition temperatures (Table 1) for the complexes are an indication of thermal stability of the compounds which might be associated with the chelation that has taken place. All the complexes are anhydrous and air stable. The Schiff base and its complexes were found to be soluble in most organic solvents (Table 4). The molar conductance (Table 3) of the complexes in dimethylsulphoxide (DMSO) was found using a conductivity meter (Jenway Conductivity meter 4010). The values was in the range 77.58-85.10 Ω⁻¹mol⁻¹cm², these large values suggest the presence of anion outside the coordination sphere. These values are in good agreement with those reported earlier (Abbas *et al.*, 2013; Geary, 1971). The magnetic moment values of the complexes obtained (Table 5) was in the range of 4.62-5.34 B.M and is an indication of paramagnetic nature of the complexes due to the presence of unpaired electrons in the partially filled d-orbitals (5, 6, 7 and 8) for Mn²⁺, Fe²⁺, Co²⁺ and Ni²⁺ respectively. The values suggest the complexes to be high spin while the spin-only values suggest an octahedral geometry for the complexes. The positive X_m value confirmed the substances to have unpaired electrons; this is in agreement with what has been reported earlier (Yousif *et al.*, 2013). Gravimetric analysis data for the complexes obtained showed that the complexes analyzed as [M(L)₂] 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 ligands (Appendix IV) revealed a stoichiometric values of M:L metal-ligand ratio. Table 2 revealed the infrared spectra of the ligand ([L] which showed a characteristic band at 1623cm⁻¹ which is attributable to ν C=N band. These bands shifted to lower frequencies range 1610cm⁻¹ - 1623cm⁻¹ in the complexes [M(L)₂]; this indicates involvement of the azomethine nitrogen in bonding, this is similar to the values reported by Nakamoto, 1971; Kolawole and Ndahi, 2004; Reddy *et al.*, 2008. The band at 3719cm⁻¹ in the ligand, [L] which is absent in the spectra of its complexes was assigned to ν O-H and could be taken as an indication of deprotonation and involvement of the hydroxyl oxygen in complexation, this is similar to Zahid *et al.*, 2009 and, Ndahi and Nasiru, 2012. The appearance in the complexes of low frequency non-ligand bands around 632-645cm⁻¹ and 533-537cm⁻¹ was assigned to ν M-N and ν M-O, similar to (Shakir *et al.*, 2006 and Shakir *et al.*, 2014). It was taken as an evidence for the coordination through nitrogen of azomethine and oxygen of -OCH₃ group of [L] with the central metal, similar to those reported by Ndahi and Nasiru, 2012. These bands was absent in the ligand. The shifting of the band at 1623cm⁻¹ in the spectra of the ligand to lower values in the spectra of the complexes, (around 632-645cm⁻¹) and the vibration centered around 3719cm⁻¹ assigned to ν O-H revealed that complexation has taken place and that azomethine and hydroxyl oxygen were involved in coordination to the metal ion, this implied that the ligand [L], was tri-dentate. The antimicrobial analysis of the compounds obtained (Tables 6), revealed that the metal complexes have higher antibacterial activity than the free ligands. This suggests that chelation increases the antibacterial activity of the compounds as reported by, (Ndahi *et al.*, 2012; Zahid and Maimoon, 2000)

CONCLUSION

The complexes have been synthesized and characterized by melting point/decomposition temperatures, solubility tests in different solvents, molar conductivity, IR spectroscopy, Jobs method of continuous variation, Gravimetric tests and antimicrobial activities. From the results of the analysis conducted on the Schiff base and its complexes, and from available literatures, it could be established that the ligand L, was tridentate. The general molecular structure proposed for the Schiff base and its metal(II) complexes is as shown in the figures below.

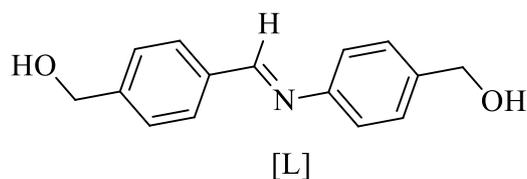


Fig. 1. Schiff base ligand, L

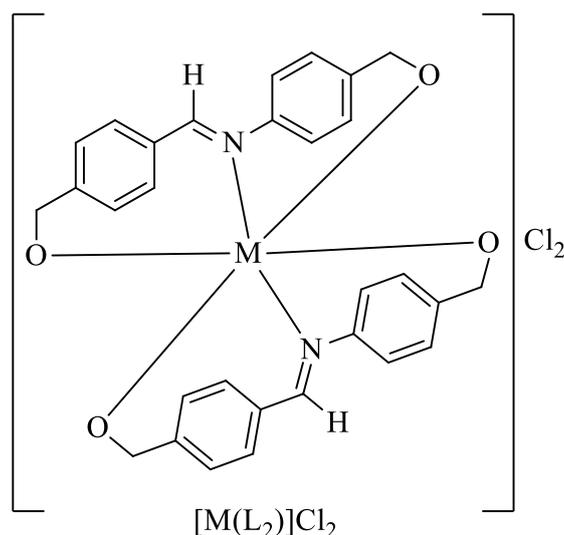


Fig. 2. Proposed molecular structure for the Schiff base complexes, [M(L₂)]
where M = Co(II), Fe(II), Mn(II) or Ni(II)

References

- 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
- Aliyu H. N, and Bilyamin U. L. (2011) Studies on bis(paraanisidineacetylacetonato)Nickel (II) Complex; *Bayero Journal of Pure and Applied Sciences*, 4(1):32-35
- Anant P, and Devjani, A. (2011) Application of Schiff bases and their metal complexes A Review. *International Journal of Chem. Tech Research*..3(4):189-196.
- Bader, N. R. (2010) Applications of Schiff's Base Chelates in Quantitative Analysis: A Review. *Rasayan J. Chem*; 3(4): 660-70.
- 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.

- Basavaraj, M. Kalshetty., Suvarnakhandi, S. S., Sheth, R. C., Hiremath, P. S., and Kalashetti, M. B. (2011) Temperature effect on solution stability constants of metal complexes with Schiff bases derived from 5-aldehydosalicyclic acid aniline and its related compounds. *International Journal of Applied Biology and Pharmaceutical Technology*, 2(2):88-93. ISSN:0976-4550
- Daniel C. Harris, (2007) Quantitative Chemical Analysis - Seventh Edition, W. H. Freeman and Company New York Pp. 629-637 ISBN: 0-7167-7041-5
- Didarul, A. C., Mohammad N. U, and Farhana H. (2011) Dioxouranium(VI) complexes of some monovalent bidentate Schiff base ligands derived from aniline *J. Nat. Sci.* 10(2): 261-268
- Feroza, H. W., Hafeez, U., Muhammad, H. S. W., Muhammad, G., Syed, A. T., Sadia, A, and Abdul Wadood, (2012) Synthesis, spectroscopic characterization and antibacterial activities of three Schiff bases derived from dehydroacetic acid with various substituted anilines, *Turkish Journal of Biochemistry*; 37(4):386- 391
- Geary, W. J. (1971) The use of conductivity measurements in organic solvents for the characterization of coordination compounds, *Coord. Chemistry Review.* 7, 8 122.
- Jain, A and Valecha, S. (2015) Synthesis and Characterization of Schiff base derived from 4-benzoyl-3 methyl-1-phenylpyrazol-5-one and *p*-anisidine. *ActaChim. Pharm. Indica*: 5(2): 55-59
- Keypour H., Rezaeivala M., Valencia L., Perez- Lourido P., Raza Khavasi H. (2009) Synthesis and Characterization of some new Co(II) and Cd(II) macrocyclic Schiff-base complexes containing piperazine moiety, *Polyhedron*, 28(17), 3755.
- Kolawole, G. A., N. P. Ndahi. (2004) Cobalt(III) complexes of dimethylglyoxime with no direct cobalt-carbon as possible non organometallic models of vitamin B12. *Synth. React. Met. Org.Chem*, 34(9):1563-1580.
- Mahmud, T. (2010) Synthesis and characterization of the amino acid Schiff bases and their complexes with copper(II). in School of Chemistry; University of Manchester, Manchester. Pp. 4-5.
- Manimekalai, R. (2011) Transition metal complexes of phenylacetates and substituted phenylacetates with neutral hydrazine as a ligand. *International Journal of Applied Biology and Pharmaceutical Technology*, 2(3):251-262
- Nakamoto, K. (1971) Infrared spectra of inorganic and coordination compounds, John Wiley and Sons, New York. Pp.125-130
- 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.
- Pallavi, G., Dinesh, K, and Sulekh, C. (2014) Schiff's base ligands and their transition metal complexes as antimicrobial agents. *Journal of Chemical, Biological and Physical Sciences*; 4(3): 1946-64.
- Reddy, V., Patil, N., Angadi, S. D. (2008) Synthesis, Characterization and Antimicrobial Activity of Cu(II), Co(II) and Ni(II) Complexes with O,N, and S Donor Ligands, *European Journal of Chemistry*, 5(3), 577-583
- Shakir, C., Kassum, H. and Alias, M. (2014) Synthesis, physical characterization and biological evaluation of Schiff base M(II) complexes, *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 15: 28-34
- Shakir, M., Azim, Y., Chishti, H and Parveen, S. (2006) Synthesis, characterization of complexes of Co(II),Ni(II), Cu(II) and Zn(II) with 12-membered Schiff base tetraazamacrocyclic ligand and the study of their antimicrobial and reducing power. *Spectrochimica Acta Part A*, 65: 490-496
- Yousif, Emad., Ahmed, Majeed., Khulood, Al-Sammarae., Nadia, Salih., Jumat, Salimon., Bashar, Abdullah. (2013) Metal complexes of Schiff base: Preparation, Characterization and Anti bacterial activity. *Arabian Journal of Chemistry*, <http://dx.doi.org/10.1016/j.arabjc.2013.06.006>
- 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.
- 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