



## SYNTHESIS AND STUDY OF THE EFFICACIES OF TETRAAZA MACROCYCLIC LIGAND FOR THE ADSORPTION OF HEAVY METALS FROM WASTEWATER

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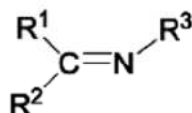
### ABSTRACT

Condensation of Ethyl 2-methylacetoacetate and ethylenediamine yield 88.7% of 5,12-Dimethyl-7,14-Diphenyl-1,4,8,11-Tetraazacyclotetradeca-4,7,11,14-Tetraene with a condense chemical formula as  $C_{18}H_{32}N_4O_2$ , and a molecular weight of 336.47. The complexes were prepared by the adsorption of heavy metals (Fe, Cu, Cd, Co and, Pb) from wastewater samples obtained from Kofar sauri, Lambun Dan Lawal and Youth craft village. The compounds were investigated by solubility, conductivity, melting/decomposition point, Atomic Absorption Spectroscopy, Infrared spectroscopy and Uv-visible spectroscopy. The Ligand 003 shows IR peak of  $\nu(C=N)$  at  $1633\text{cm}^{-1}$ , and a shift was observed to a lower peak as a result of adsorption of the heavy metals by the ligand, which is signifying the formation of the complexes. AAS results indicates high concentration of Cu in each case when compared, the rest of the metals varying at different level of concentration in the compounds. Cu may best fit the center of the ligand cavity having a concentration beyond computing with the rest of the metals.

**Key words:** Schiff base, wastewater, heavy metals

### INTRODUCTION

Schiff bases are important class of ligands that are obtained as a result of a coordination of a metal ion, via azomethine nitrogen, and are extensively being studied (Raman *et al.*, 2001). Structurally, Schiff base (also known as imine or azomethine) is a derivative of a ketone or aldehyde where the carbonyl group (C=O) is being replaced by an imine or azomethine group (Figure. 1) (Kalaivani *et al.*, 2012). Schiff base ligands are important in the field of coordination chemistry, especially in the advancement of complexes, because they usually formed stable compounds (complexes) with metal ions (Souza *et al.*, 1985)



$R^1, R^2,$  and/or  $R^3 =$  alkyl or aryl

Figure 1: General structure of Schiff bases (Silva *et al.*, 2011)

Cyclic Schiff bases that generally contain organic frames into which hetero atoms, capable of binding to substrates, are interspersed, are called Macrocylic ligands

(Van, 1943). Macrocycles have many interesting properties, part of which is include their efforts to attack "difficult" targets with extended binding sites. Because of their size and complexity, they can employ targets through several and spatially distributed binding interactions, which increase both their binding affinity and selectivity. (Chaudhary and Rawat, 2014)

Water pollution is one of the major hazardous environmental problem, that concern the world at large. Water pollution arises when pollutants are discharged into water bodies, either directly or indirectly (Owa and F.D 2013, Mann *et al.*, 2011).

The harmful effects of heavy metals to the environment and public health is a matter that always requires a global attention. Heavy metals in water bodies are one of the most significant environmental complications faced by many developed and developing countries. The increase of industrial and other environmental activities, highly contributes to the significant rise of heavy metal contamination in water resources, thereby making threats on terrestrial and aquatic life.

The toxicity of metal pollution is slow and interminable, as these metal ions are non-bio-degradable (Salehzadeh 2013). The treatment of heavy metals in wastewater and drinking water is employed to reduce the heavy metal concentration to the acceptable level. Many conventional methods are available with a varying degree of attainment to remove heavy metals ions from wastewater. They include chemical solvent extraction (Gupta *et al.* 2007), precipitation (Esalah *et al.*, 2000), ion exchange (Lin *et al.* 2008), filtration (Bessbousse *et al.* 2008), reverse osmosis (Benito *et al.*, 2002), and adsorption (Aguado *et al.*, 2009).

Organic-based ligands that give out stable coordination compounds has been suggested as a substitute procedure for the extraction and removal of dissolved heavy metals from polluted water. (Quan *et al.*, 2003, Dede *et al.*, 2009) Some of the main properties of a suitable extracting agent include; high affinity toward the target metals and their ability to react with a series of metal ions, and produce stable insoluble compounds (Freiria *et al.*, 2006). The paper demonstrated the use of a macrocyclic ligand, in removal of heavy metals from wastewater, obtained from Kofar sauri (K/sauri), Lambun Dan-Lawal (LDL) and Youth Craft Village (YCV), sited within Katsina local government area of Katsina state.

#### MATERIALS AND METHODS

All reagents used were of analytical grade, obtained from Zayo-Sigma and Qualikems and used without extra purification. All weighing was done on an electrical meter balance. Melting point/decomposition temperatures were determined using IA9000 series digital melting point apparatus while conductivity measurements were conducted using HI-2300 conductivity meter, pH was conducted using a pH HI-99121 meter, AAS was conducted using Flame atomic absorption spectrophotometer. IR measurements were recorded using Shimadzu FTIR spectrophotometer.

#### Synthesis of the Macrocyclic Schiff Base (003)

A hot ethanolic solution (20ml) of ethyl 2-methylacetoacetate (2.89g, 0.02mol) and 20ml ethanolic solution of ethylenediamine (1.20g, 0.02mol) were mixed with continuous stirring. The mixture was refluxed at 80°C ( $\pm 5$ ) for 6

hours in the presence of few drops of conc HCl (pH<sub>2</sub> 3-4). The progress of the reaction was followed using a paper chromatography. Upon cooling, a yellow colored compound was precipitated, filtered, washed with cold ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. As shown by scheme 1. (Rehman *et al.*, 2014) The Schiff base was analyzed by IR, Uv-visible spectroscopy, solubility, and melting point, as shown by table 2-5

#### Wastewater Sample Digestion for Metal ions Determination

To each 50cm<sup>3</sup> of the waste water, (YCV, LDL, and K/sauri), 5ml of 65% HNO<sub>3</sub> was added, and then the mixture was boiled gently for 30-45min. After cooling, 2.5ml of 70% HClO<sub>4</sub> was added, and the mixture was gently boiled until dense white fumes appeared. Later the mixture was allowed to cool and 10ml of deionized water was added followed by further boiling until the fumes were totally released. Finally, the sample was taken for AAS as shown by figure 2-4 (Hussein, 2014). Note: Similar procedure was employed, in the digestion of the complexes after adsorption of the metal ions by the ligands. The result is shown by figure 5-7

#### Adsorption of the Heavy Metals by the Ligands

The heavy metals were extracted by mixing the hot methanolic solution of the ligand with the wastewater, and refluxed for 3 hours. The heavy metals present in the wastewater were detected using AAS. (Hussein, 2014)

#### Adsorption Procedure

100cm<sup>3</sup> of the wastewater containing the heavy metals obtained from Youth Craft Village (YCV) was enriched (concentrated) to 50cm<sup>3</sup> and agitated vigorously with 1.0g of the ligand (s), in a stoppered glass conical flask, and placed on a mechanical shaker for 30min, the mixture was stirred for 2 hours, and refluxed by dissolving in ethanol-water mixture (40:60) at 80°C ( $\pm 5$ ) for 6 hours, and finally left standing for an additional 2 hours. Upon cooling, a colored compound was precipitated, filtered, and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. The concentration of the heavy metals in the compounds were determined using AAS. The procedure was repeated with two other forms of waste water obtained from Lambun Dan Lawal (LDL), and Kofar Sauri (K/sauri) irrigation sites. (Hussein, 2014)

## RESULTS AND DISCUSSION

The macrocyclization of the Schiff base was made by introducing symmetrical connections at the NN positions, with removal of water molecules, as shown by scheme 1, which is expected to increase the stability of the corresponding complexes (Martinez *et al.*,

2005). The ligands act as a tetradentate ligand with the lone pairs on the nitrogen atoms of the azomethine (Ilhan *et al.*, 2007). The reaction was followed progressively using a paper chromatographic technique, to ensure the formation and the purity of the compound, only one spot was observed (Omar, 2007).

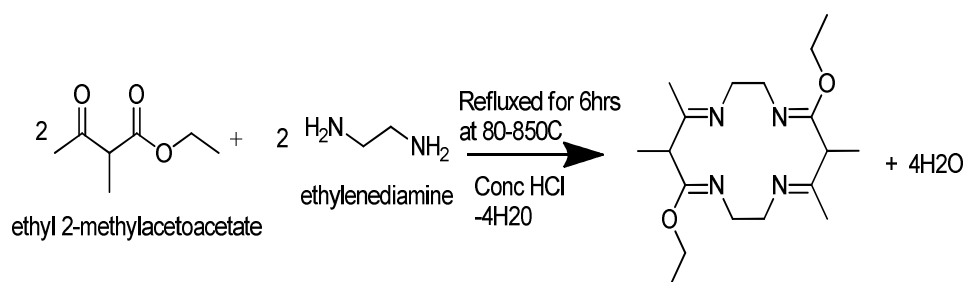
1. Synthesis of C<sub>18</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub> (003)

Table 1: Wastewater Physical Analysis and the Heavy Metals Present

S/N	Wastewater samples	Color	PH	Heavy Metals Present
1	Kofar Sauri (K/sauri)	Colorless	6.8	Cu, Fe, Co, Cd and Pb
2	Youth Craft Village (YCV)	Dark Purple	6.6	Cu, Fe, Co, Cd and Pb
3	Lambun Dan Lawal (LDL)	Colorless	6.8	Cu, Fe, Co, Cd and Pb

Table 1 shows a physical analysis and some of the heavy metals present in the three wastewater samples. K/sauri and Lambun Dn Lawal wastewater samples show similarity in color and pH, while Youth Craft Village has a different color and the most acidic pH value, and this might be due to some industrial

activities taking place within the area. The acidic nature of the three wastewater samples might be due to the presence of the heavy metals. The heavy metals can only be minimized to some acceptable concentrations. (Esalah *et al.*, 2000)

Table 2: UV-visible spectroscopic analysis of the wastewater and the Compounds

S/N	Wastewater and the Compounds	$\lambda_{\text{max}}(\text{nm})$	Electronic Transition
1	Kofar Sauri	250	$n \rightarrow \sigma^*$
2	Youth Craft Village	250	$n \rightarrow \sigma^*$
3	Lambun Dan-Lawal	200	$n \rightarrow \sigma^*$
4	003	400	$n \rightarrow \pi^*$ , $\pi \rightarrow \pi^*$
5	(003 + K/sauri) Complex	600	$\pi \rightarrow \pi^*$
6	(003 + LDL) Complex	550	$\pi \rightarrow \pi^*$
7	(003 + YCV) Complex	550	$\pi \rightarrow \pi^*$

Key: (Code 003) is C<sub>18</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>

Table 2 shows a  $\lambda_{\text{max}}$  within the range of 200-250nm for all the wastewater samples, which is signifying  $n \rightarrow \sigma^*$  electronic transition, which might be due to the presence of non-bonding electrons on the oxygen of the water molecule. The Schiff base and the complexes, displays an

intense absorption within the range of 400-600 attributed to  $n \rightarrow \pi^*$  (due to lone pairs) and  $\pi \rightarrow \pi^*$  (due to C=N) for the Schiff base and  $\pi \rightarrow \pi^*$  (due to C=N) for the complexes (Ahmed *et al.*, 2014).

**Table 3: Physical data of the synthesized ligands and their complexes**

S/N	COMPOUND	M.P/D.T	CONDUCTIVITY	PHYSICAL STATE	COLOUR
1	003	120	-	Solid	Yellow
2	(003 + K/sauri) Complex	192	102	Solid	Orange
3	(003 + LDL) Complex	192	110	Solid	Yellow Orange
4	(003 + YCV) Complex	192	59	Solid	Army Green

**Key:** (Code 003) is  $C_{18}H_{32}N_4O_2$

In table 3 the ligand appeared to be yellow colored solid, with a sharp melting point (Xavier and Srividhya, 2014). The change in color of the ligand after reflux, from yellow to (orange, yellow orange and army green) complexes can be termed as an indication of the heavy metals adsorption. The compounds show variability in colors and, molar conductance values as shown by table 3. Omar (2007), reported variable colors of conventional Schiff bases and, their corresponding complexes

formed from a Schiff base and a metal salt, in a similar way displayed by table 3. The melting point of the ligand and decomposition points of the metal complexes shows variability, as shown by table 3, which indicated their possible thermal stability. The molar conductance measurement of the complexes in DMSO falls in the range  $59-110 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in Table 3, which indicates electrolytic nature of the compounds.

**Table 4: Solubility test of the ligands and their metal complexes**

S/N	Compound	DMSO	DMF	MeOH	EtOH	Acetone	Chloroform	Diethyl Ether	Benzene
1	3	S	S	SS	S	S	SS	IS	IS
2	(003 + K/sauri) Complex	S	SS	SS	S	S	IS	IS	IS
3	(003 + LDL) Complex	S	S	S	SS	S	SS	IS	IS
4	(003 + YCV) Complex	S	S	SS	S	SS	IS	IS	IS

**Key:** (Code 003) is  $C_{18}H_{32}N_4O_2$ , S = Soluble, SS = slightly soluble, IS = Insoluble

The solubility test in table 4 showed that; the ligands and their metal complexes exhibit different behavior in some common solvents. Some of the compounds were found to be soluble in methanol and ethanol and others

slightly soluble. The ligand and its metal complexes were found to be soluble in dimethyl sulphoxide (DMSO), this might possibly be due to the high dielectric constant of the solvent (Sani and Baba, 2016).

**Table 5: Infrared Absorption Frequencies ( $\text{cm}^{-1}$ ) of the Ligands and their Metal Complexes**

S/N	Compounds	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$
1	003	1633	—
2	(003 + K/sauri) Complex	1547	462
3	(003 + LDL) Complex	1585	466
4	(003 + YCV) Complex	1599	462

**Key:** (Code 003) is  $C_{18}H_{32}N_4O_2$

FTIR spectra of the ligand and its metal complexes were recorded in KBr medium in  $200-4000\text{cm}^{-1}$  range, to identify the ligands formation, strength of metal-ligand bonds in the complexes, and to monitor their bonding vibrational modes (Mohammed *et al.*, 2015).

Table 5 showed the azomethine  $\nu(\text{C}=\text{N})$  peak at  $1633\text{cm}^{-1}$  in the IR spectrum of the ligand. (Ilhan *et al.*, 2007; Hussein 2014). The IR spectra of the complexes and ligands plays an important role, in displaying the structure of the compounds.

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The IR spectra of the complexes when compared with those of the ligand, indicated that the  $\nu(\text{C}=\text{N})$  stretching vibration band that fall within the range of  $1500\text{-}1700\text{cm}^{-1}$  is shifted to lower frequencies in all complexes (Mohammed 2015). The appearance of new

medium intensity bands within  $430\text{-}470\text{cm}^{-1}$  region, is assignable to M-N stretching vibration, is signifying the participation of the azomethine nitrogen in coordination (Omar 2007; Nakamoto 1970)

**AAS RESULTS**

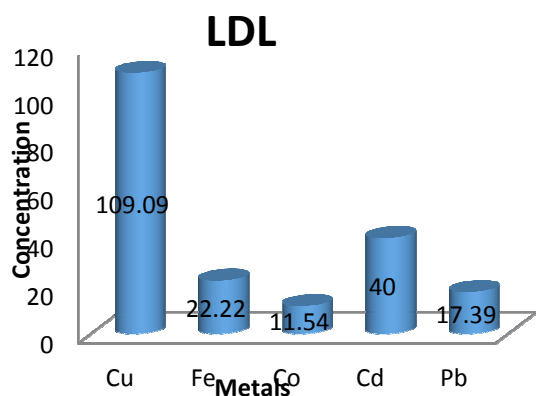


Figure 2: Lambun Dan Lawal Wastewater Sample

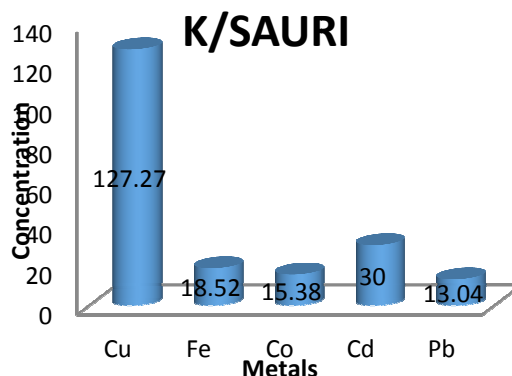


Figure 3: Kofar Sauri Wastewater Sample

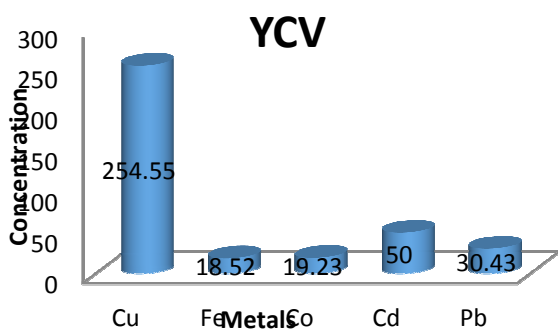


Figure 4: Youth Craft Village Wastewater Sample

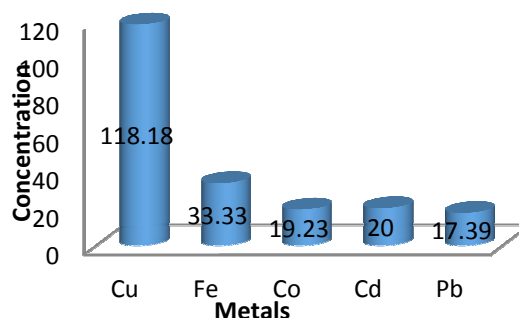


Figure 5: ( $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_2$  + K/sauri) Complex

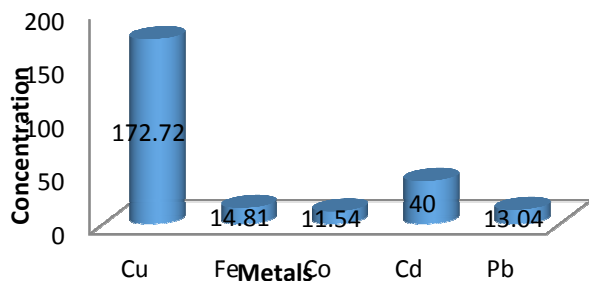


Figure 6: ( $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_2$  + LDL) Complex

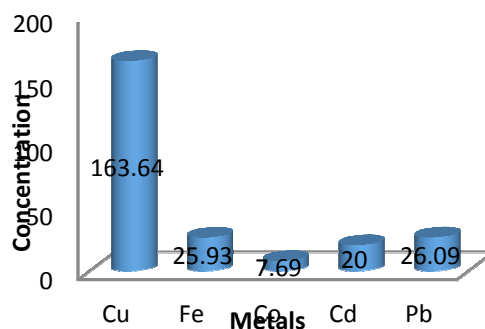


Figure 7: ( $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_2$  + YCV) Complex

The adsorption of the metal ions from the wastewater sample by the ligand ( $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_2$ ) and, formation of the complexes was studied by AAS, as shown by figure 5 to 7, and the results

proposed the complexing agents to have high affinity for the analyzed metals (Martínez *et al* 2013).

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The elements or heavy metal ions analyzed were Fe, Cu, Cd, Co and, Pb, in each case Cu ions shows the highest concentration. Figure 2 to 4 shows the concentration of the metals in every 100cm<sup>3</sup> of the wastewater samples, which is aerated to remove microbes and enriched (concentrated) the volume to 50cm<sup>3</sup>. Shureshkumar and Milind, 2013 reported concentration among other major factors that influence the adsorption, for that; the highest expectation is placed on Cu ions at the center of the macrocyclic Schiff bases cavity. Additionally, the order of affinity of the metals towards the ligand may assumed to have followed Irving Williams series, in which selectivity and stability of the complexes could be related to the ionic radius of the metals, because of the affinity showed by Cu (Martínez *et al.*, 2013). Comparing of the complexes in terms of concentration, order of adsorption and affinity of the ligand (003) to the metal ions indicates that; Cu>Fe>Cd>Co>Pb, Cu>Pb>Fe>Cd>Co and Cu>Cd>Fe>Pb>Co when refluxed with the wastewater from K/sauri, Lambun Dan Lawal and Youth Craft Village

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respectively, although Cu has the highest concentration in each case.

### CONCLUSION

The macrocyclic Schiff base was prepared as reported, and a very stable complexes were formed via adsorption of heavy metals present in wastewater samples obtained from Kofar sauri, Lambun Dan Lawal and Youth Craft Village. This was investigated by characterizations such as solubility, conductivity, melting/decomposition point, IR, Uv-visible and AAS. Where the azomethin bond formed, shows a shift to a lower frequency, and the appearance of metal nitrogen bond within the reported range. AAS reveals the presence of five (5) heavy metals or ions namely; Fe, Cu, Cd, Co and, Pb, where in each case, Cu has the highest concentration when compered. Research is currently going on, on some Schiff bases with the same wastewater samples for easy comparison.

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