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Synthesis and Characterization New Schiff Base Derivatives and Their Complexes with Zn (II) and Ni (II)

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Abstract: *In recent years, discovering new compounds that have biological activity were studied by many researchers. In this paper, four metal complexes have been synthesized from Ni (II) and Zn (II) chloride and ligands 2-((3-nitrophenylimino) methyl) phenol (HL1) and 2-((4-nitrophenylimino) methyl) phenol (HL2) in 1:2 M ratio. FTIR and molar conductance measurements were used to characterize the structure of complexes. The complexes were found to be non electrolytic on the basis of molar conductance studies. The metal complexes have also been tested for their PH activity at different concentrations by used RSM.*

***Keywords**: Metal complexes, Schiff bases, RSM*

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I. Introduction

The discovery and development of antibiotics and pesticides are among the most powerful and successful achievements of modern science and technology for the control of infectious diseases. The most spectacular advances in medicinal chemistry have been made when coordinating compounds played an important role in regulating biological systems.

Synthesis of Schiff bases and their metal complexes having novel structural features and unusual physicochemical properties have considerable importance in biological processes (Kumar *et al* 2009) and constitute an active area of research in modern coordination chemistry.

Schiff bases have a number of synthetic uses in organic chemistry such as acylation of Schiff bases by acid anhydrides, acid chlorides and acyl cyanides, which is initiated by attack at the nitrogen atom and leads to net addition of the acylating agent to the carbon-nitrogen double bond. Reactions of this type have been put forward for natural product synthesis.

Intramolecular hydrogen bonding between OH and –C=N- atom of Schiff base determines the properties of various molecular systems and plays a significant role in many biochemical mechanism (Chelmienieckaet *al* 2001). Since proton transfer is known to be crucial for physicochemical properties and practical application of Schiff bases, therefore, this process has been widely studied in literature. Intramolecular electron transfer is a fundamental chemical phenomenon that relates specifically to redox processes that occur in both natural and synthetic electron-transfer system. Schiff bases show a wide range of biological activities such as antimalarial, anticancer, antibacterial (Lakhe and Mangaonkar 2012), antifungal, antitubular (Hilmy et al 2012), anti-inflammatory (Dave and Bansal 2013), antiviral, antifertility and antipyretic activities (Prakash and Adhikari 2011). They also show nematicidal activity (Jain et al 2002, Al-Kahraman et al 2011, Kundu et al 2009) but could not be exploited to their potential in pest control due to long period of time required for completion of the reaction and are not stable compounds as these get easily disintegrated when exposed to moisture. To overcome this problem, their metal complexes have been synthesized which generally show better activity than their corresponding ligands. Binding of metal ions with polydentate ligands form ring structure, where the metal ion is a part of the ring, is called chelation. By using catalyst, the time taken by the reaction in conventional method can be reduced and the product can be utilized upon industrial level as become cost effective.

It is fact that copper, iron, zinc and cobalt are essential metallic elements at different PH and exhibit great biological activity when associated with certain metal protein complexes, participating in oxygen transport, electronic transfer reactions or the storage of ions has created enormous interest in the study of system containing these metals. The interaction of transition metal complexes with DNA has been extensively studied in the development of new tools for nanotechnology. Antioxidants are extensively studied for their capacity to protect organism and cell from damage that is induced by oxidation stress.

II. Experimental

a. The Preparation of Ligands

Weight 5g of 2 (3-nitrophenylimino) then add 4ml of salysaldehyde and 40 ml of absolute alcohol (methanol) as catalyst after that leave the solution from 2 to 3 h until the solid product is formed then filter the solution to get the ligand as crystals powder and wash it by using diethylether "the recrystalization process is done by hot solution of (Ethanol)".

Weight 5g of 2(4-nitrophenylimino then add 4ml of salysaldehyde and 40 ml of absolute alcohol (methanol) as catalyst after that leave the solution from 2 to 3 h until the solid product is formed then filter the solution to get the ligand as crystals powder and wash it by using diethylether "the recrystalization process is done by hot solution of (Ethanol):

The chemical equations of this reaction

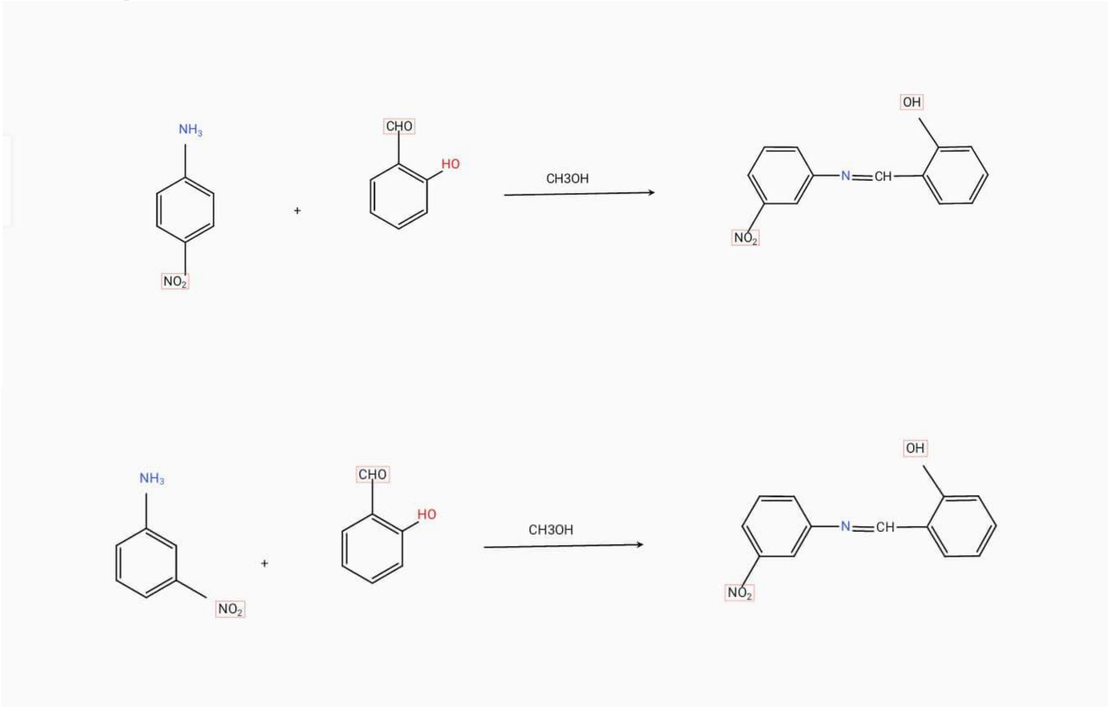


Figure.1synthesis of Schiff base compound

Figure 2 Preparation of ligands

b. General producer steps to synthesis the metal complexes

The complex formation is done by weighting 0.25g of metal chloride (Zncl2 /Nicl3) and dissolve it in solution of methanol after that prepare solution of 0. 5g of the ligand that is completely dissolve in hot solution of absolute alcohol then mix it together leave the complex solution up to the stairing heater for 1-2 hours until the color change then filter it to get the complex as a precipitate.

The reaction represented by these equation:

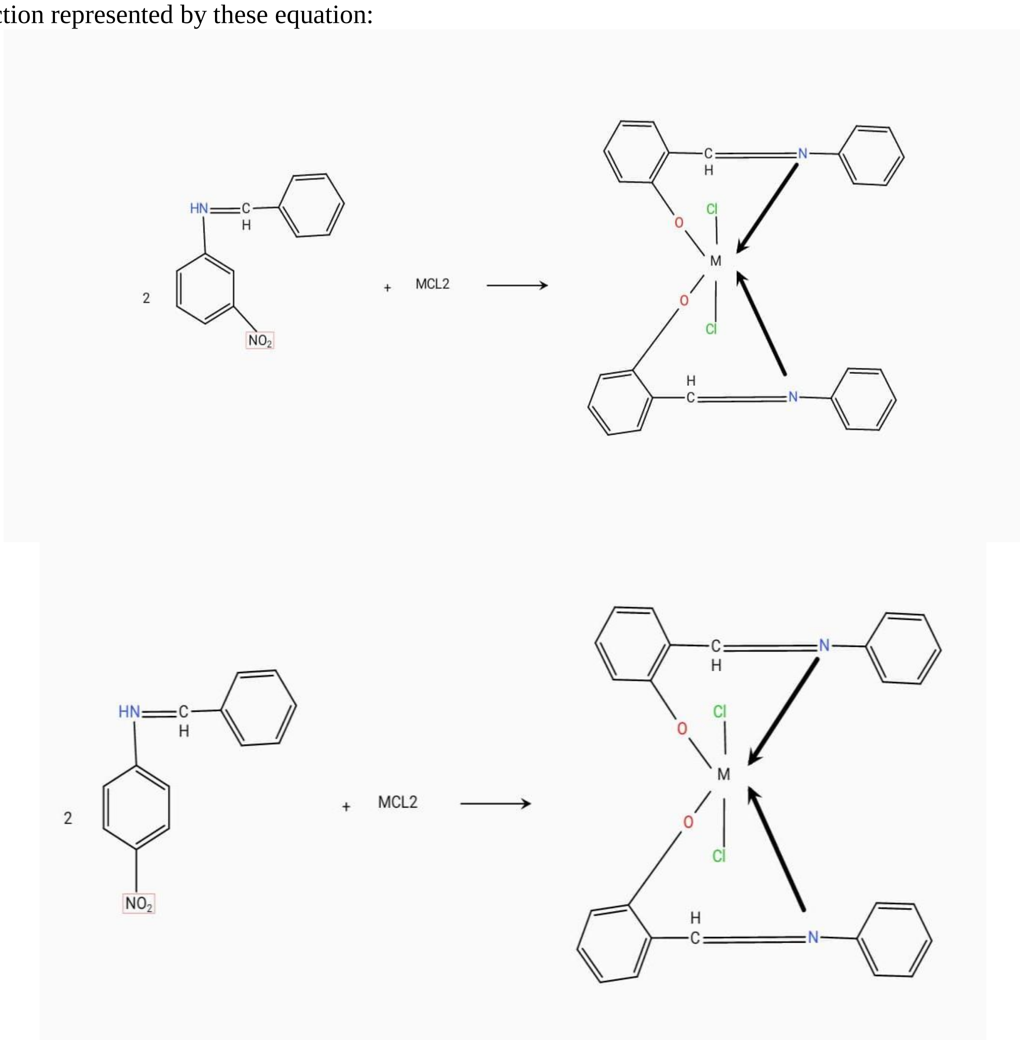


Figure Error! No text of specified style in document. synthesis of metal complexes 2:1.

Figure 4 Preparation of complexes

c. Titration of Complexes

Full the burette by NaOH then weight 0.001g of the metal complex after that add 1ml of NaCL and 1ml of HCl with stairing add droply 5ml of sodium hydroxide then 15ml to the complex solution and at each volume measure the PH value by using the PH meter.

Full the burette by NaOH then weight 0.003g of the metal complex after that add 1ml of NaCL and 1ml of HCl with stairing add droply 5ml of sodium hydroxide then 15ml to the complex solution and at each volume measure the PH value by using the PH meter. Full the burette by NaOH then weight 0.002g of the metal complex after that add 1ml of NaCL and 1ml of HCl with stairing add droply 10ml of sodium hydroxide then 17ml to the complex solution and at each volume measure the PH value by using the PH meter.

Study The effect of PH using RSM

The main objective of PH measurement was to determine the value of PH at different concentration metal complexes. In the experimental different concentration from metal complexes was applied and titration by NaOH where the number of experimental was constructed according to design matrix attained from the Response Surface Method (RSM). Finally, 3 D RSM was applied to investigate the effect of wiegt of metal complexes on the PH measurement.

As a rule, RSM was employed to solve problems requiring a few parameters with restricted ranges, similar to the ones investigated in this PH measurement. RSM comprises of three stages. First, it requires a succession of experiments, i.e., Designs of Experiments (DoE). The experiments are to ensure that the results yield sufficient, dependable measurements of the response required. Finally, the 3D of RSM are established.

The estimation procedure of this approach is shown in Figure 3.8; the desired objective was the PH measurment which was determined as the response. The wiegt complexes and NaOH that were supposed to influence the PH measurment were selected to investigate the PH measurement. Experiments based on the PH measurment for each run were performed according to the design matrix based on the central composite design (CCD). RSM provided a design matrix containing 6 numbers of runs, and then the 3D of RSM was performed to investigate the relationship between the factors and responses

III. Results And Discussion

Synthesis of metal complex by react the Schiff base with Ni and Zn After the complex synthesis process was completed some measurements were made as (mp – conductance –FTIR – PH) and the result will discussed as following:

a. Melting point measurements

Table .1 shows the measurements of the melting point for each complexes and ligands which obtained via the melting point device.

Table.1 Melting point of complexes and ligands

Complex	Melting point
Ni complex 1	169 C^0
Ni complex 2	144 C^0
Zn complex 1	168 C^0
Zn complex 2	136 C^0
Schiff base 1(m)	134 C^0
Schiff base 2 (p)	163 C^0

b. The conductivity of metal complex

Table .2 shows the conductivity results for each complex and ligands using the conductivity meter LF91.

Table.2 The conductivity of complexes

Complex	Conductance value (ms/cm)
Ni complex 1	0.026
Ni complex 2	0.030
Zn complex 1	0.030
Zn complex 2	0.020
Schiff base 1(m)	0.010
Schiff base 2 (p)	0.010

c. PH Measurement based on RSM

The Weight of complex and the volume NaOH were selected in this study for further investigation their influence on the PH measurement. The measurement of the PH range of each complex at certain volume has been measured based on the RSM to minimize the number of experiments where the weight of complex and the volume NaOH were selected as independent parameters while the PH measurement was selected as the response of complex concentration.

The Weight of complex and the volume NaOH were changed based on the central composite design (CCD). Furthermore, to minimize the influence of the extraneous parameters, all of the experiments were performed in randomized orderTabulation of the arrangement of the central composite design. The arrangement of the CCD, responses, and their values from the experimental results are listed in Table 4.3.

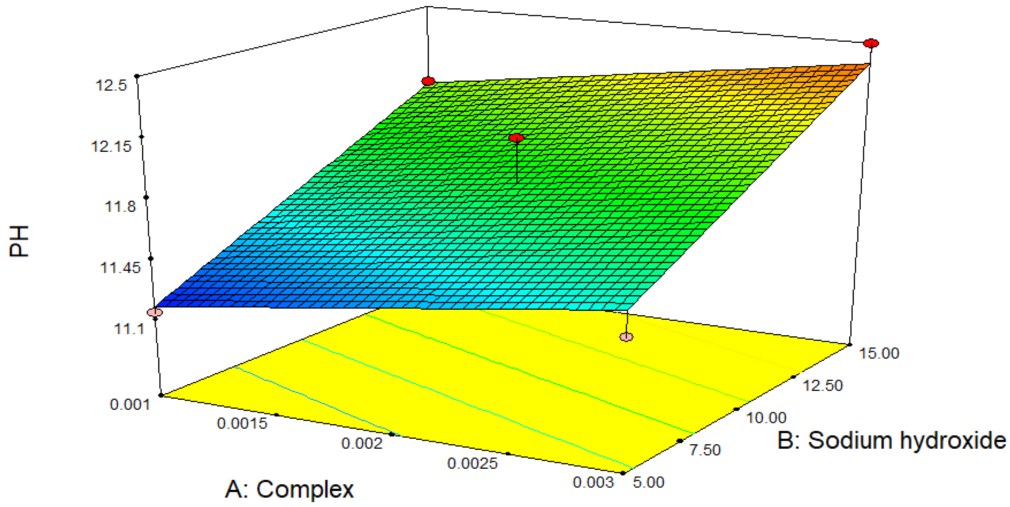
Table.3 Central composite design arrangement, responses and their values for experimental results of the PH values of complexes

		Independent factors (actual value)		Response
Metal complexes	Run	Factor 1 Weight(mg)	Factor 2 Volume NaOH (ml)	PH
Ni Complex 1	**1**	1	5	11.14
	2	3	5	11.4
	3	1	15	12.02
	4	3	15	12.5
	5	2	17	12.22
	6	2	10	12.05
Ni Complex 2	**1**	1	5	12.3
	2	3	5	11.4
	3	1	15	12.2
	4	3	15	12.2
	5	2	17	12.9
	6	2	10	13.5
Zn Complex 1	**1**	1	5	7
	2	3	5	11.71
	3	1	15	7.1
	4	3	15	12.4
	5	2	17	12.7
	6	2	10	13.4
Zn Complex 2	**1**	1	5	12.5

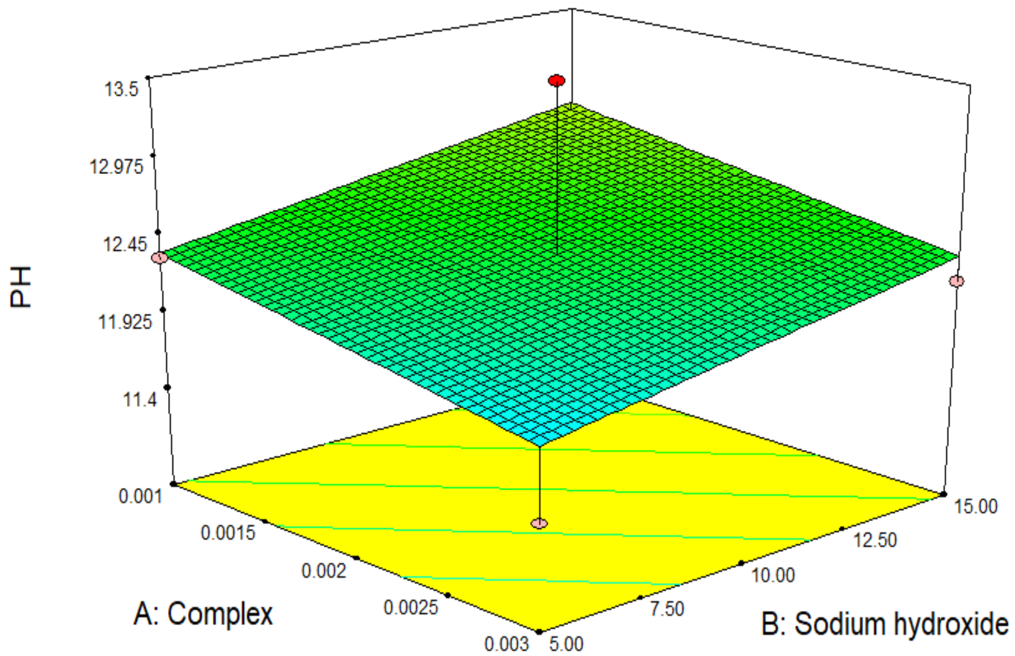
2	3	5	11.2
3	1	15	12.56
4	3	15	12.3
5	2	17	12.85
6	2	10	13.50

1. The effect of Weight Complexes ofNi 1 and Ni 2 on the PH

Figure. 5 shows the response surface 3D plots with contour plots on their bases for the PH measurement as a function of the weight complexes and NaOH. Figure. 5 (a) shows the results for Ni complex 1, and Figure 5 (b) shows the results for Ni complex 2. In general, these plots are useful to visualize the effects of the process factors and their interactions on the PH and the optimal process conditions. The designs provided the results, for Ni complex 1 where the PH measurement increased with the increase in the weight complex and for Ni complex 2 the PH measurement increased with the decrease in the weight complex. Figure. 5 shows that for, the influence of the weight complex of Ni 1and Ni 2 were significant on the PH measurement.



(a)

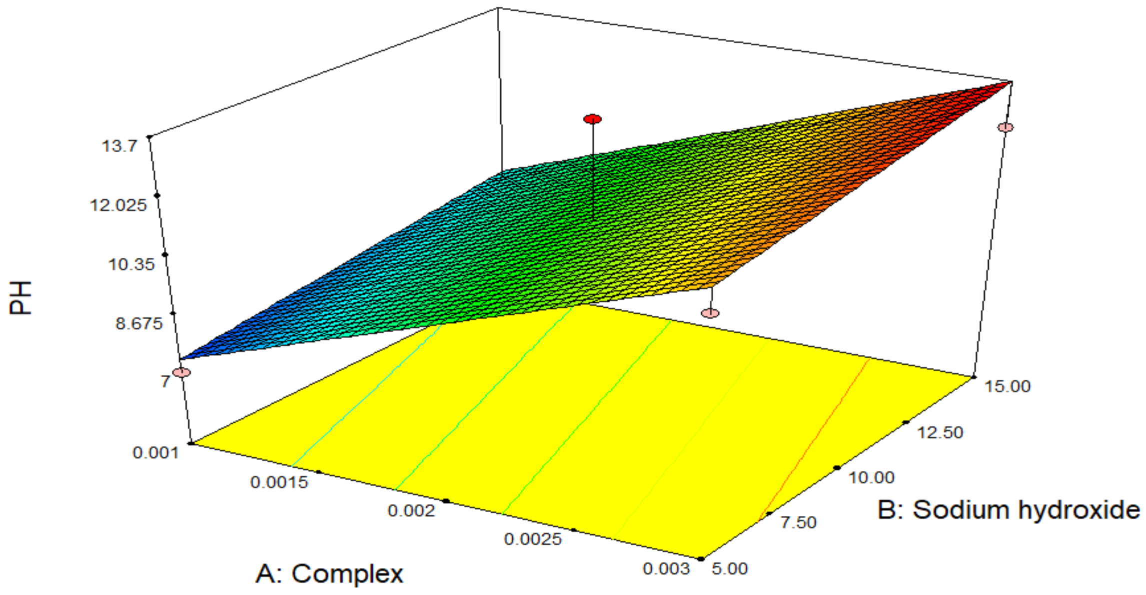


(b)

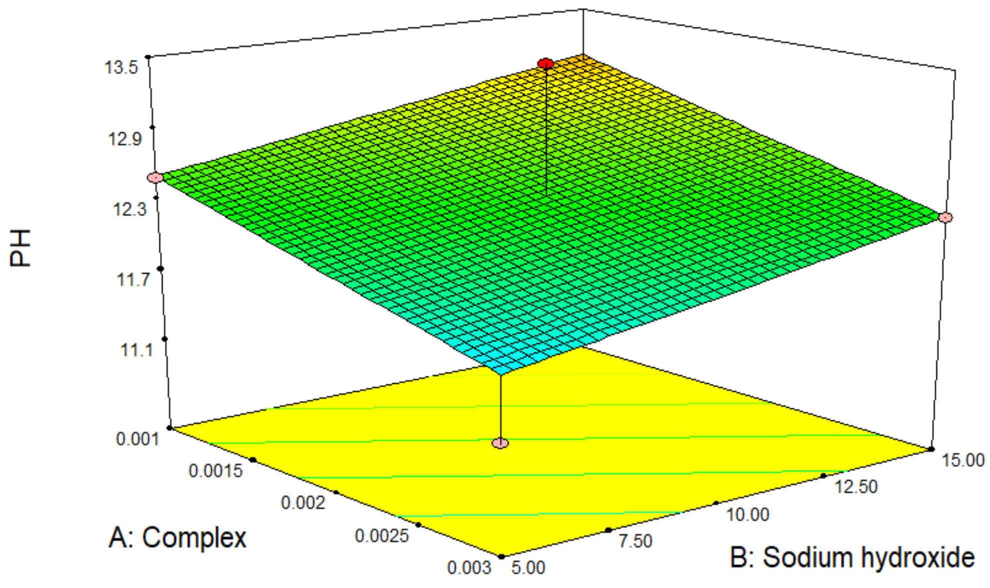
Figure 53D graphic surface of the PH as influenced by the wieght complexe of (a) Ni 2-(3-nitro phenylimino aniline)phenyl methyl, and (b) Ni (4-nitro phenylimino aniline) phenyl methyl

2. The effect of Weight Complexes ofZn 1 and Zn 2 on the PH

With the Zn complex 1 and Zn complex 2, the increase in the PH measurement was evident, as shown in Figure 6 (a) and (b). The interactive effect of the weight complex on the PH was more significant compered to Ni complex 1 and Ni complex 2. These result was explained by the positive effect of the weight complexes on the PH measurement.



(a)



(b)

Figure 63D graphic surface of the PH as influenced by the weight complex of (a) Zn 2-(3-nitro phenylimino aniline)phenyl methy (b) Zn 2-(4-nitro phenylimino aniline)phenyl methyl .

d. FTIR Measurement

Fourier Transform Infrared Spectroscopy, FTIR used to characterization of the Schiff base derivatives and their complexes in research center in Cairo.The important functional groups that should be present in compounds are the aromatic group, NO_2 group, C=C group and C-H group. This can be seen as shown in Figures, and we can see that all of the mentioned functional groups above are present. The stretching vibration of the NO_2group appeared at 3500-.3200cm^{-1}. The band appearing at 1620-1680 cm^{-1} is assigned to the stretching vibration of the C=C group, and the band appearing at 1050-.1150 cm-1 is assigned to the stretching vibration of the group C-H. By using FTIR spectroscopy we got these result of each ligands and complexes as shown in Figure 7 tile Figure 4.12.

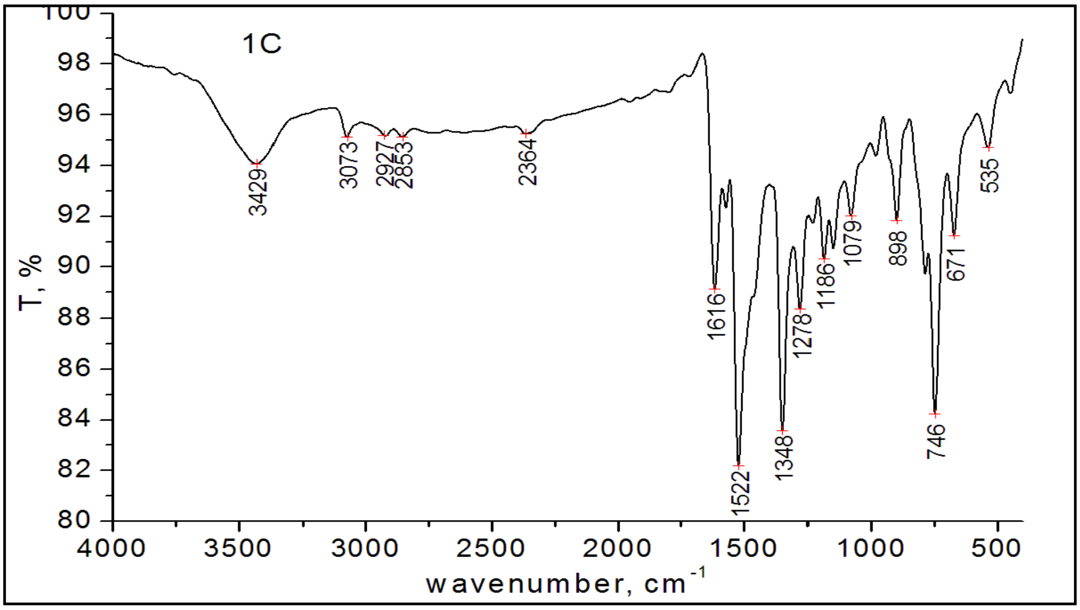


Figure 7 Ni 2-(3-nitro phenylimino aniline)phenyl methyl

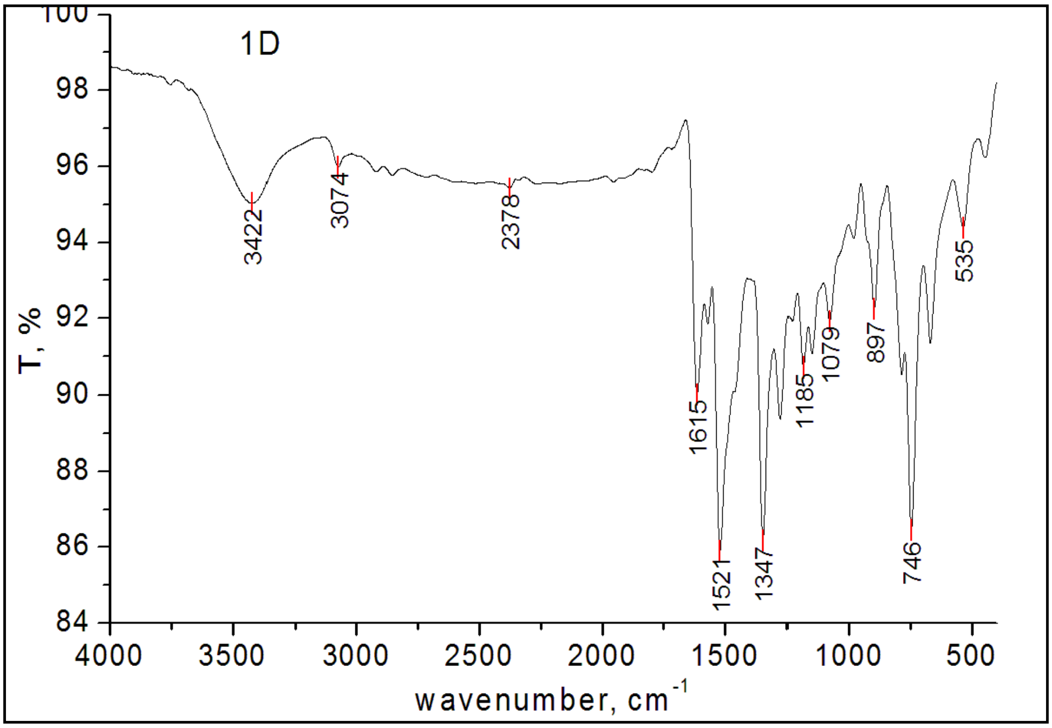


Figure 8 Ni 2-(4-nitro phenylimino aniline)phenyl methyl

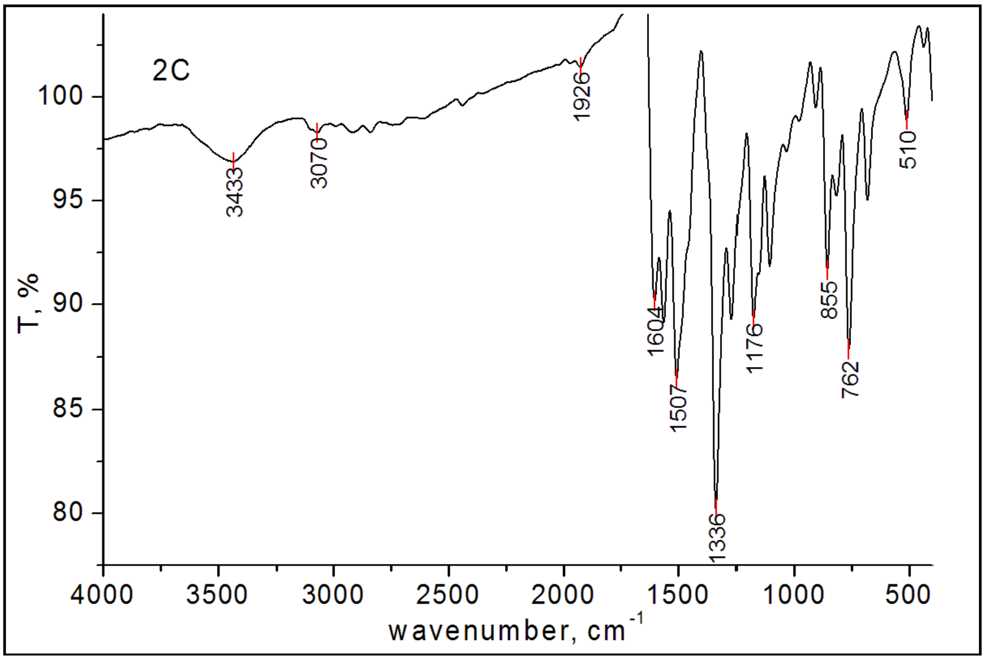


Figure 9 Zn 2-(3-nitro phenylimino aniline)phenyl methyl .

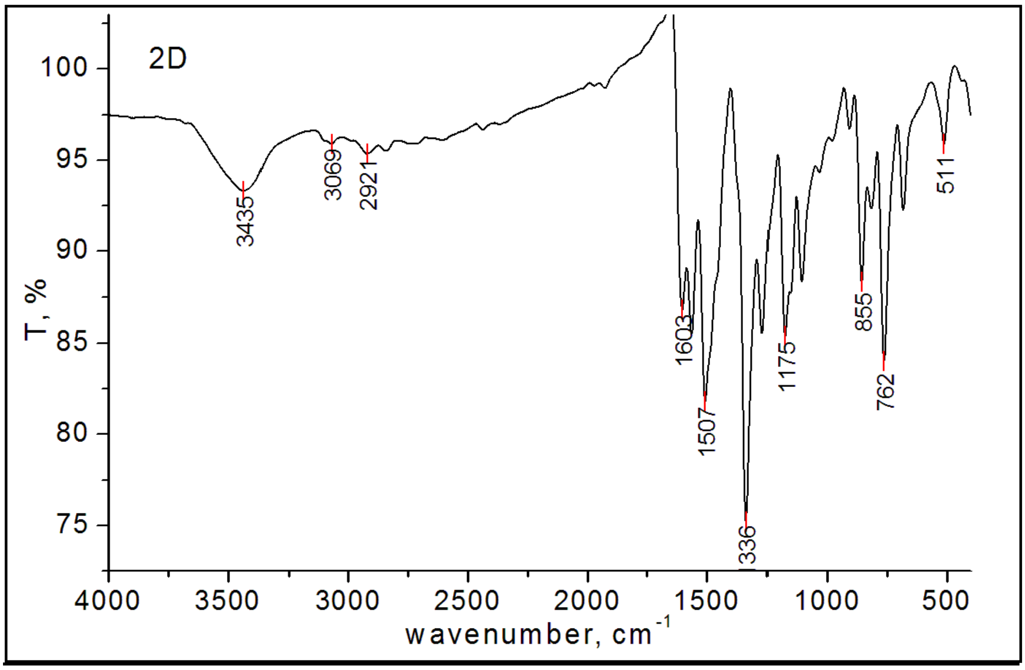


Figure 10 Zn 2-(4-nitro phenylimino aniline)phenyl methyl

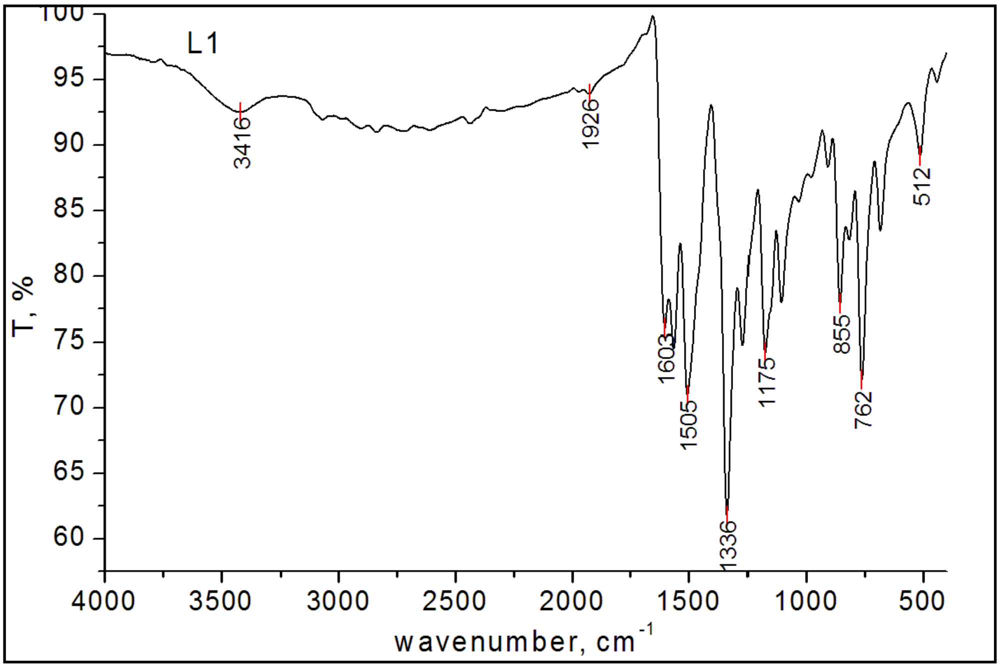


Figure 11 2-(3-nitro phenylimino aniline)phenyl methyl

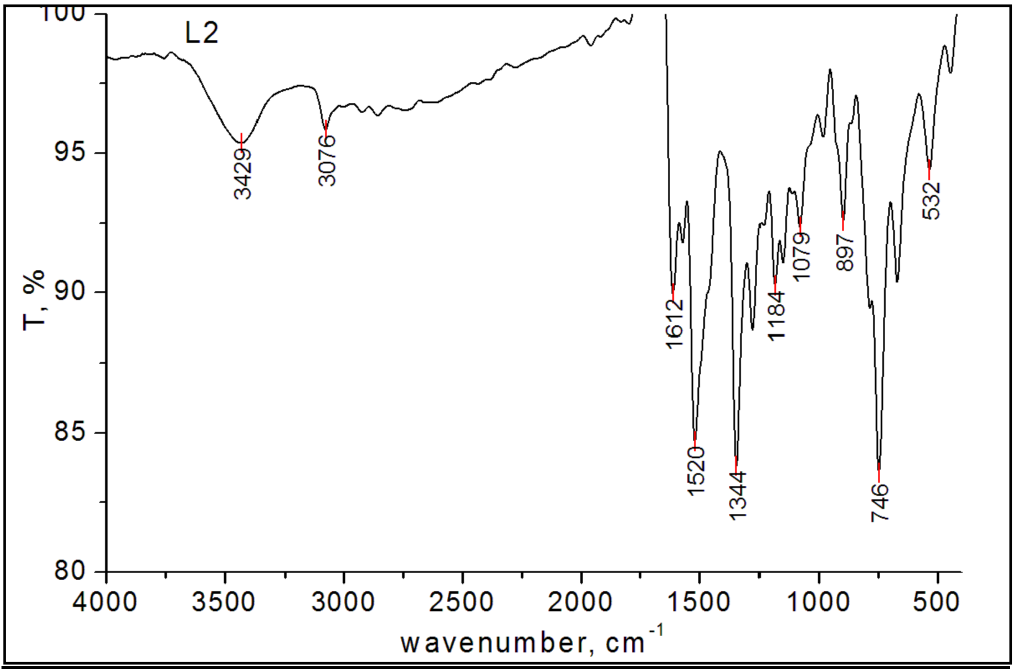


Figure 12 2-(3-nitro phenylimino aniline)phenyl methyl

IV. Conclusion

In this paper, four metal complexes have been synthesized from Ni (II) and Zn (II) chloride and ligands 2-((3-nitrophenylimino) methyl) phenol (HL1) and 2-((4-nitrophenylimino) methyl) phenol (HL2) in 1:2 M ratio. The metal complexes have also been tested for their PH activity at different concentrations using RSM. FTIR and molar conductance measurements were used to characterize the structure of complexes.These compounds has biological activity. However, more work should be done to further widen the application of the proposed compounds. For instance, synthesize more new derivatives Schiff base and synthesize their complexes with other transition metals are of considerable interest due to their structural diversity. Meanwhile, the aforesaid transition metal Schiff base complexes are of interest due to their significant cytotoxic activities in vitro such as anti-cancer screening.

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