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Synthesis, Characterization and Biological Study of New Azo -Schiff Ligand type N_2O_2 and It's Divalent Metal Ion Complexes with Zinc, Cadmium and Mercury

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Abstract

The new Azo-Schiff ligand type N_2O_2 have been prepared through two steps. The first one Included the reaction between one equivalent of P-Phenoxy aniline and one equivalent of Salcyldehyde salcildihyde to prepare azo compound .and second step include the reaction of azo compound with tri ethylene tetra amine in order to prepare the new Azo-Schiff ligand. The ions metal of Zn^{+2}, Cd^{+2} and Hg^{+2} with the new azo-Schiff ligand Complexes were prepared with mole ratio (1:1) (M: L) the prepared compounds were characterized by FT-IR, UV-Vis, while ^{1}HNMR spectra were taken for the new ligand and it complex with mercury, Elemental analysis, as well as the molar conductivity and magnetic successptibility for all prepared complexes. These measurements showed that complexes of Cadmium and Zinc have octahedral shape, and tetrahedral for Mercury complex. The biological activity was evaluated against two kinds of bacteria, gram positive and gram negative for the new Azo-Schiff ligand and it's complexes with Zn^{+2}, Cd^{+2} and Hg^{+2}.

Key Words: P-Phenoxy aniline, Salcyldehyde, triethylenetetraamine, spectra measurements, biological study.

Introduction

Azo compounds are characterized by the presence of azo group (-N=N-) [1]. the aromatic azo compounds were identified to be more stable than the aliphatic one .[2]
Azo have large importance in syntheized organic compounds, [3] aromatic used as acid - base indicators such as methyl red [4] and in synthesis of cosmetics, drugs and azodyes, while aliphatic azo can be used as radical initiators in polymerization of alkanes to make plastic.[5] This compounds show a variety of interesting biological activities including antibacterial , anticancer and antifungal .[6,7,8] on the other hand Schiff bases are compounds which contain an azomethine group (-CH=N-) [9], they are named after Schiff who prepared a number of these bases via condensation of aromatic or aliphatic aldehydes or ketones with primary aromatic or aliphatic amines [10, 11] and amino acids [12] ,these compounds are consider as starting materials for prepration of a large number of heterocaclic compounds [13] ,

and used to prepare super-conducting polymers [14] , all so have avariety of biological actions .[15,16]

Material and Equipment

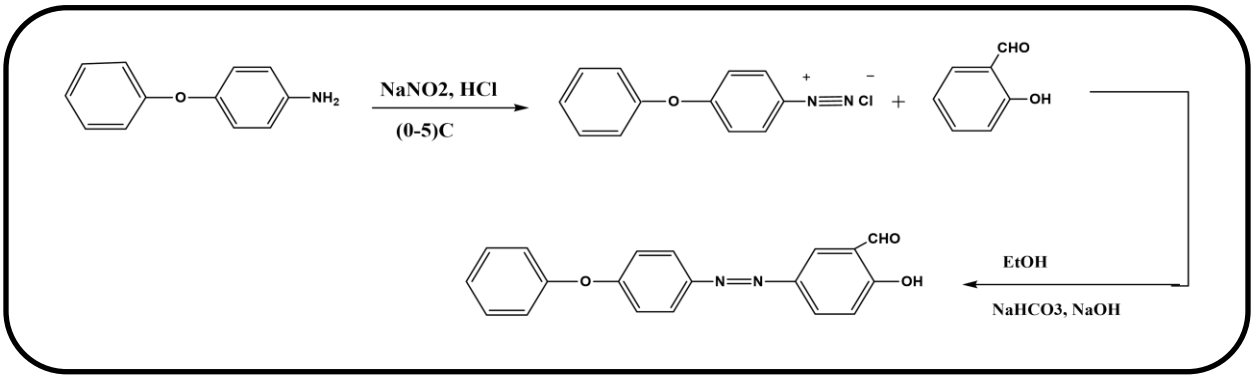
All chemicals used from Merek, Aldrich and Fluka have enough purification.
Melting point were measured by (electro thermal) melting point apparatus FT-IR spectra measured with Shimadzu FT-IR-4800S infrared spectrophotometer by using KBr disk, ^{1}H-NMR spectra by used Broker- 400 MHz –Germany with DMSO-d^{6} solvent . UV-Visible spectra recorded by UV-Visible spectrophotometer -1800 Shimadzu , and Digital Conductivity meter – WT- 720 – inolab (Germany) was used to measure the electrical conductivity .

Synthesis of The New Azo Schiff Ligand H_2L

This new ligand was prepared by two steps:

a- Synthesis of Azo Compound (C)

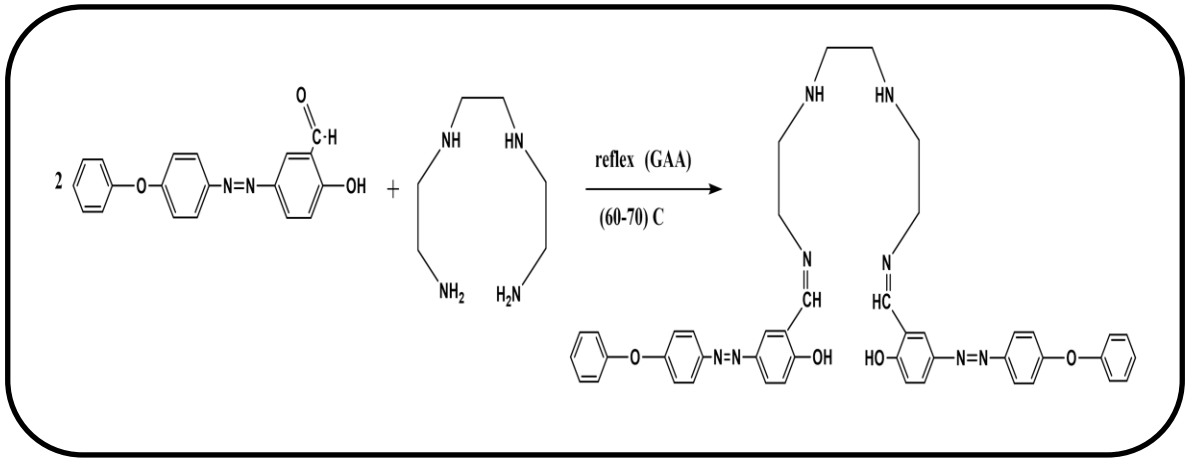
Azo compound prepared by solution of (0.01mol ,1.85 gm) P-Phenoxy aniline dissolved in (3ml HCl+ 20 ml D.W.) was added a solution contain (10 ml D.W + 0.7 gm $NaNO_2$) in ice bath (0-5)° C to prepar diazanium salt [17], then add slowly (0.01mol, 1.2 ml) of Salcyldehyde dissolve in 50 ml EtOH with [0.3gm of NaOH+ 5ml D.W. + 2 gm of $NaHCO_3$] , leave the final solution for (30) min. , filter and wash by D.W. , dry the (deep green) product , m.p (>300)ºC yield 78.7 %



Scheme. 1- Synthesis of azo compound (C)

b- Synthesis of the new Azo- Schiff Ligand H_2L

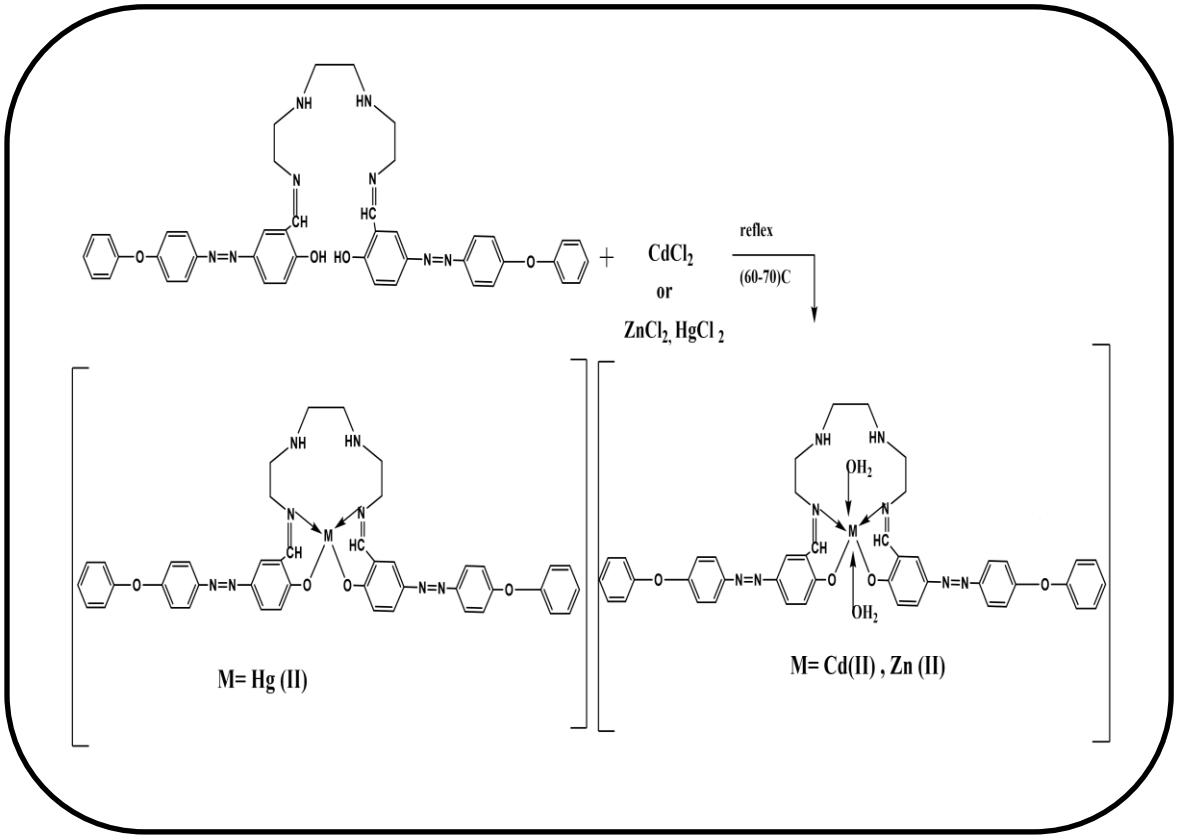
Dissolve (0.001mol , 0.302 gm) of azo compound (C) in (20ml of EtOH + 2 drops of (GAA) , then added (0.01mol, 1.5 ml) of (tri ethyl tetra amine) , reflex the mixture for (6) hours in (60-70)ºC, filter and recrystallization with hot ethanol ,dry the (Light brown) final product .



Scheme. 2- Prepare of Azo- Schiff Ligand H_2L

Synthesis of Chelate Complexes with New Azo- Schiff Base Ligand

The solid complexes prepared by addition (0.001mol) of metal chloride of Cd(II), Zn(II) , Hg(II) to a solution of (0.001mol, 0.744 gm) for ligand dissolve in (35 ml) hot ethanol , then reflex the mixture for (2) h in (60-70) ºC , the prepared products washed with D.W. [18].as in scheme3.



Scheme.3- Prepare of Azo- Schiff Ligand H_2L Complexes

Some physical properties and data of elemental analysis for the new azo- Schiff base ligand and it's chelate complexes were recorded in table1.

table. 1- Some physical properties and analytical data of the new azo- Schiff base ligand and it's complexes .

No.	Compound	Wt. formula	color	m.p .ºC	Yield %	Calc. (Found)%			
						%C	%H	%N	%M
1	$H_2L_3=C_{44}H_{40}N_8O_4$	744.32	Light Brown	291-295	85.3	70.95 (70.77)	5.41 (5.11)	15.04 (15.25)	…
2	$[ZnC_{44}H_{38}N_8O_4(H_2O)_2]$	844.25	Light Brown	Dec.264	84.2	62.60 (62.39)	5.01 (5.34)	13.27 (13.11)	7.74 (7.91)
3	$[CdC_{44}H_{38}N_8O_4(H_2O)_2]$	891.28	Brown	>300	80.9	59.29 (59.42)	4.74 (4.50)	12.57 (12.88)	12.61 (12.92)
4	$[HgC_{44}H_{38}N_8O_4]$	943.43	Grey	>300	80.6	56.02 (55.72)	4.06 (4.40)	11.88 (11.50)	21.26 …..

Resuits and Discussion

FT-IR Spectra

The FT-IR spectra for ligand H_2L_3 figure (1) show a stretching vibration bands that belong to phenolic υ (O-H) in 3400 cm^{-1} and υ (N-H) in 3363 cm^{-1}(seen browd band due to interaction between υ (O-H) and υ (N-H) bands) , [19] aliphatic υ ($-CH_2$) in 2928 cm^{-1} and aromatic υ (-CH) in 3100 cm^{-1} , weak υ(CH=N) band in 2200 cm^{-1} and a vibration in 1676 cm^{-1} belong to υ(C=N) band , υ(N=N) band in 1429 cm^{-1} .[20]

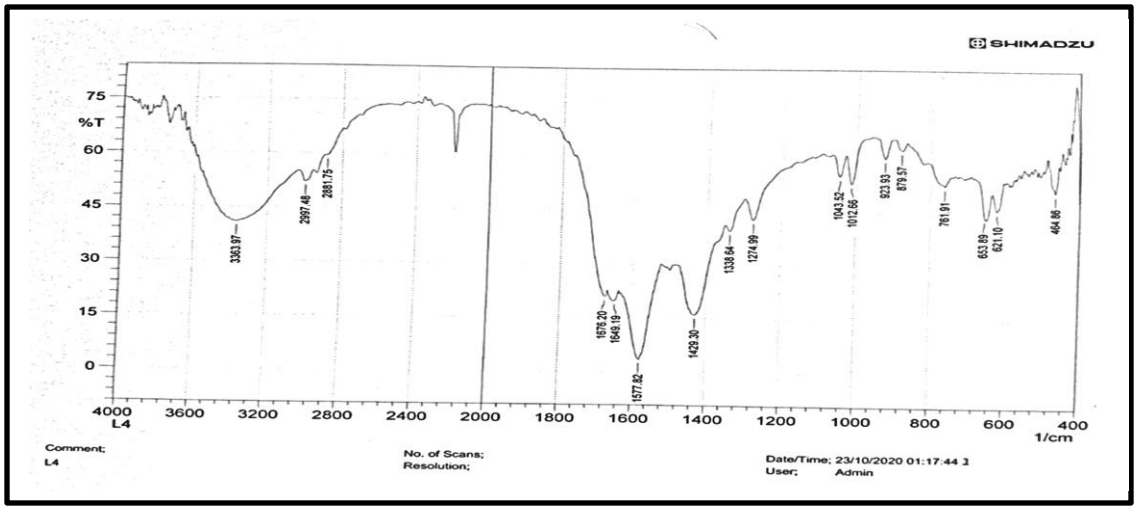


Fig.1- FT-IR for Azo- Schiff Ligand

while the FT-IR spectra for complexes figures 2 , 3 , 4 show disappear phenolic υ(O-H) and different shift for υ (N-H) between (3454-3304) cm $^{-1}$,aromatic υ (-CH) between (3080-3173) cm $^{-1}$ and υ(-C=N) between (1614-1680) cm $^{-1}$, in the other hand , new bands were appear like υ (O-H) of water between in (3500-3458) cm^{-1} and in finger print area between (894-854) cm^{-1} for cadmium and zinc complexes respectively . in addition, υ(M-N) [21] and υ(M-O) for all complexes, between (460-474) cm $^{-1}$and (501- 572) cm $^{-1}$ respectively All the infrared frequencies of the azo- Schiff base ligand and their complexes are given in table 2.

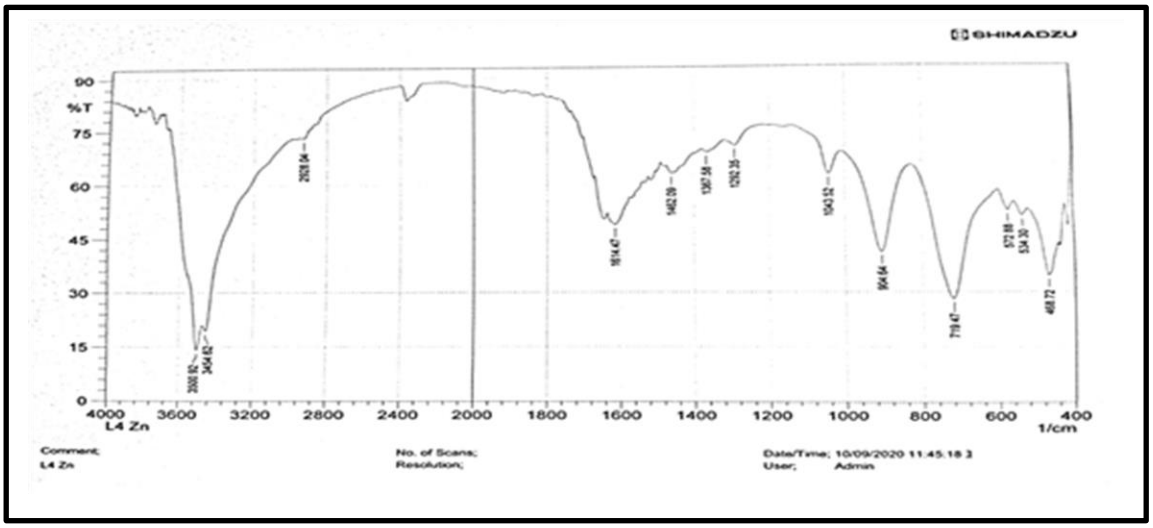


Fig.2- FT-IR for Zinc complex

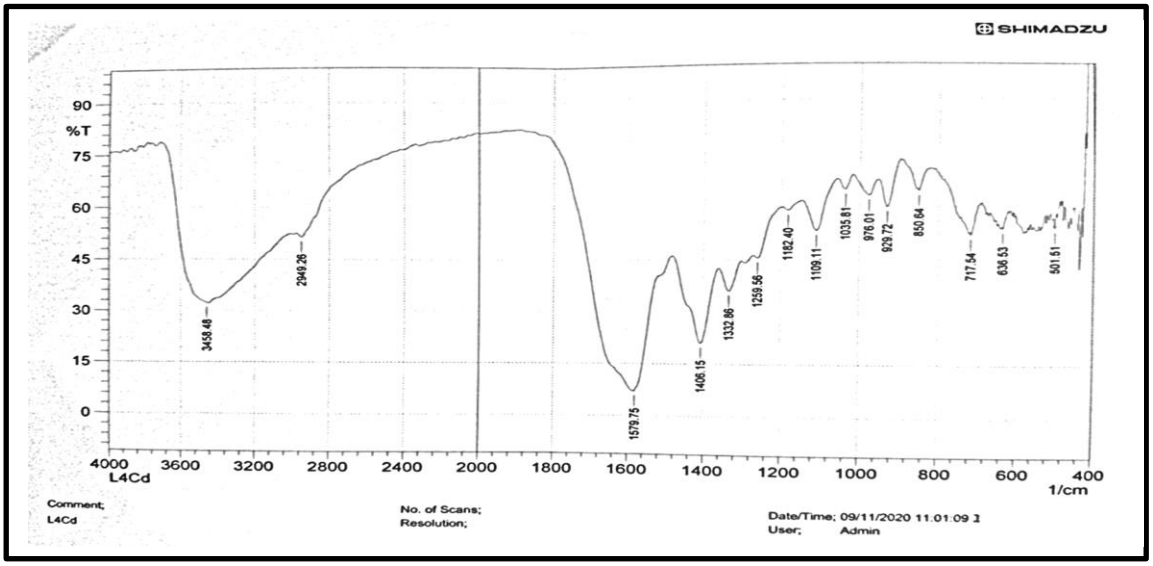


Fig.3- FT-IR for Cadmium complex

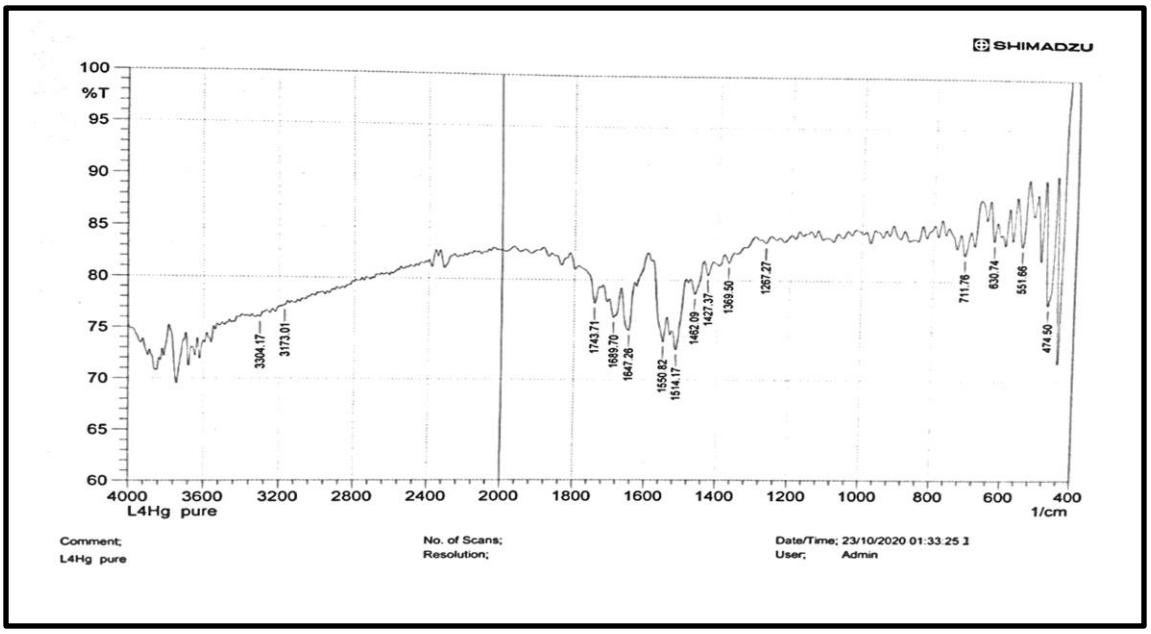


Fig.4- FT-IR for Mercury complex

table.2 - FT-IR spectral data (cm^{-1}) of azo-schiff base ligand and it's complexes

Comp.	υ(O-H) phenolic	υ(O-H) water	υ(N-H)	υ(C-H) aromatic	υ(C-H) aliphatic	υ(CH=N)	υ(C=N)	υ(N=N)	υ(M-O)	υ(M-N)
H_2L	3400	……	3363	3120	2997	2200	1676	1429	……	……
[ZnL $(H_2O)_2$]	…….	3500	3454	3100	2928	2340	1614	1462	572-534	468
[CdL $(H_2O)_2$]	…….	3458	3360	3080	2949	2280	1680	1406	501	460
[HgL]	…….	…….	3304	3173	2950	2300	1647	1462	551	474

UV-Visible Spectra

The electronic absorption spectra of the new azo-Schiff base ligand and it's complexes were recorded in absolute ethanol solution (1×10^{-3}) M at room temperature .

The electronic spectrum of ligand fig. (5) showed two bands in (ʎ =312) nm (32051.28) cm^{-1} and (ʎ =381) nm (26246.72) cm^{-1} belong to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [22]

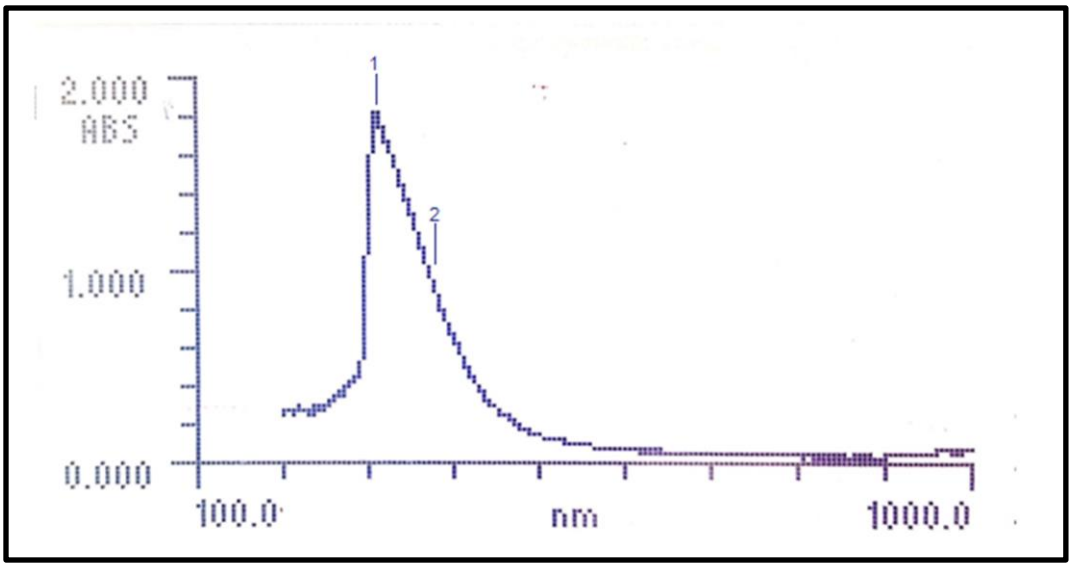


Fig.5- UV-Vis for azo- Schiff ligand

when we compared it with UV -Vis spectra of complexes have noticed the differences , The Zn (II) complex ,fiq-6 is Light brown in colour exhibits one absorption band at (ʎ= 328) nm (30487.80) cm^{-1}, identified for charge transition (C.T.) this indicate the present of an octahedral geometric structure of Zinc (II) complex. The spectrum of Cd(II) , complex fig- 7 is brown in colour exhibits two absorption bands at (ʎ= 328) nm (30487.80) cm^{-1} identified for charge transition (C.T.) and (ʎ= 429) nm (23310.02) cm^{-1} due to (M.L.C.T.) transition. and Hg(II) complex fig- 8 grey in colour showed two absorption bands at (ʎ= 330) nm (30303.03) cm^{-1} assigned to a charge transfer transition, (ʎ= 432) nm (23148.14) cm^{-1} due to (M.L.C.T.) transition. no (d-d) field transition band but always shows (C.T.) transition . all complexes are diamagnetic moment because prossess completely filled d^{10} configuration . based on this data , an octahedral geometry for Cd(II) complex and tetrahedral geometry for Hg(II) complex [23].

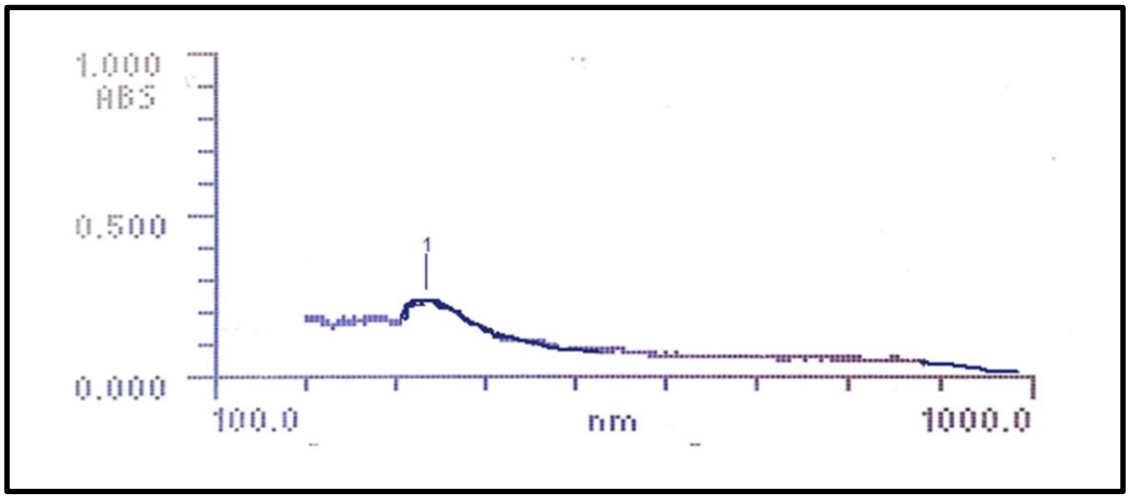


Fig.6- UV-Vis for Zinc complex

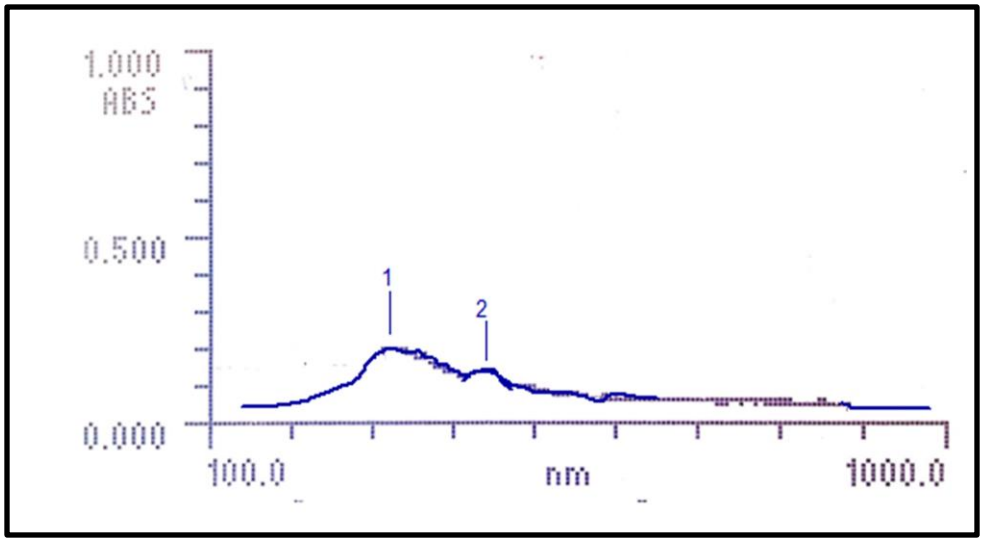


Fig.7- UV-Vis for Cadmium complex

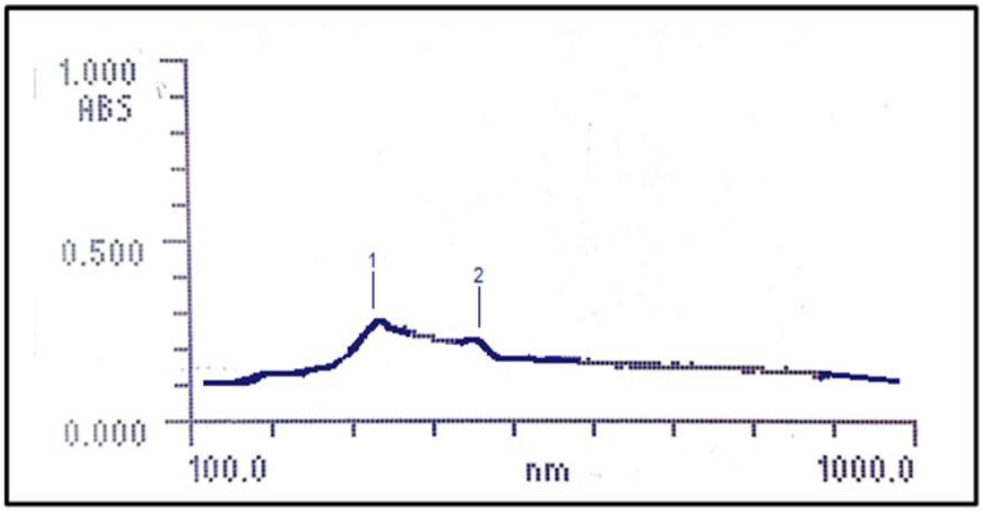


Fig. 8- UV-Vis for Mercury complex

^{1}H-NMR Spectra for Ligand and [HgL] Complex

^{1}H-NMR data for compound H_2L and Hg (II) complex are show in fig-9 and fig-10 was recorded by using DMSO-d^6 as a solvent and the chemical shift in (2.50 ppm) .for ligand, the singlet signal of NH protons was appeared in (δ= 1.69 ppm,2H) [24], and the multiple signal of aromatic rings protons in range (δ= 6.4-7.8 ppm,24H), the singlet signal of phenolic protons (-OH) appeared in (δ= 8.5 ppm, 2H),.[25] peaks of (-CH_2) groups belong to aliphatic amine appear in range (δ= 3.67- 2.53 ppm, 12H), and singlet signal at (δ= 8.0 ppm, 2H) due to isomethine groups (H-C=N) protons. While in Hg (II) complex have different shifting in signals.

The position phenolic (-OH) protons is disappear in the spectra of Hg (II) complex indicating the involvement in bonding between Hg (II) and ligand with absence proton .[26]

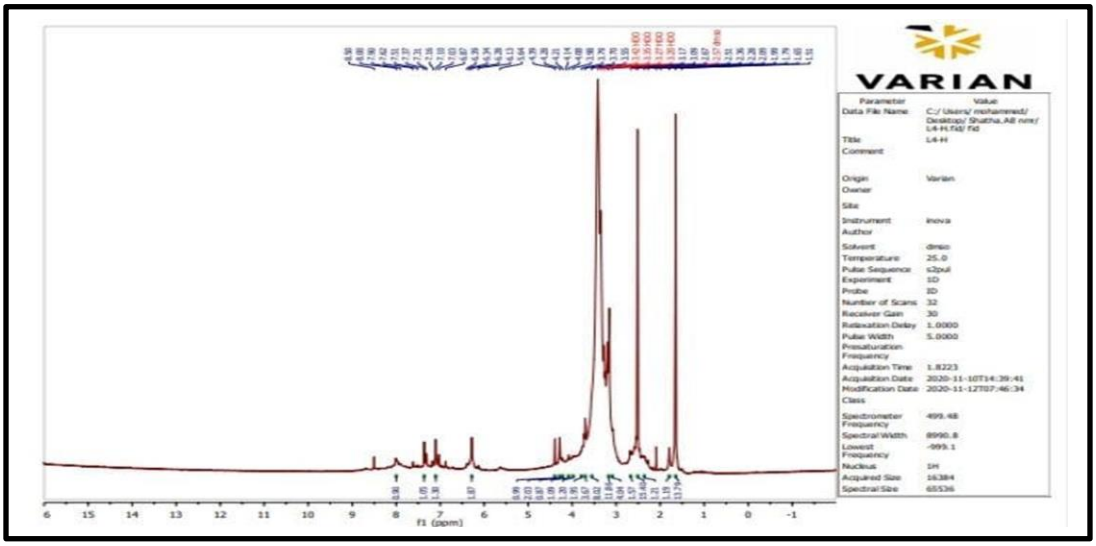


Fig.9- ^{1}H-NMR Spectrum for Ligand H_2L

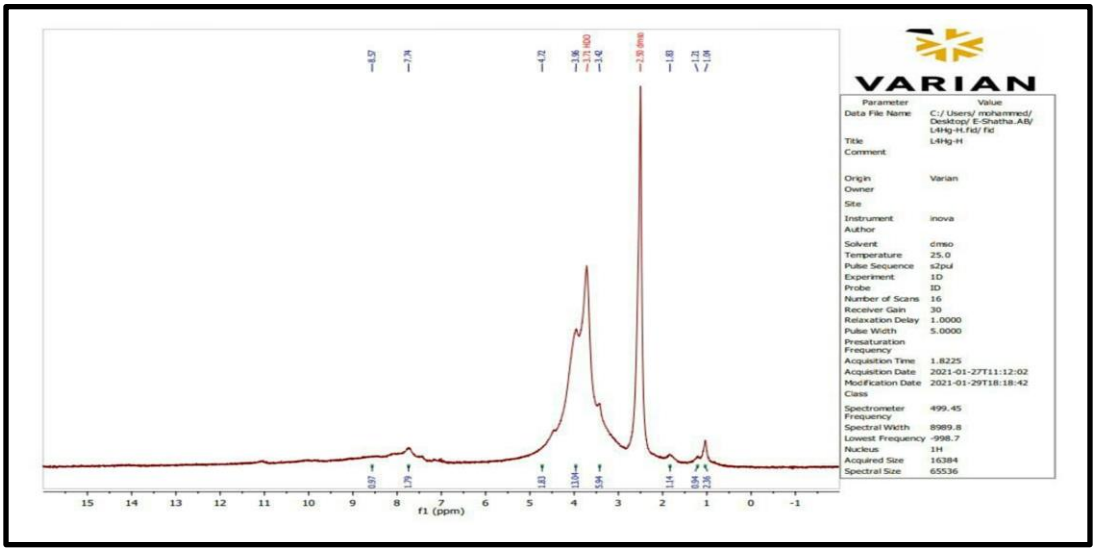


Fig.10- ^{1}H-NMR Spectrum for Hg(II) Complex

Magnetic susceptibility and molar conductivity

The magnetic properties of complexes were measured by faradi method and shows that complexes Zn (II) , Cd (II) and Hg (II) are diamagnetic [27] , and the molar conductivity of the complexes was recorded in EtOH solvent [28] appears that all complexes were non-

electrolyte, supported with octahedral geometry for Zn (II) , Cd (II) and tetrahedral geometry for Hg (II) complexes. as show in table (3).

table.3- Magnetic Susceptibility and Molar Conductivity for Complexes

compound	Magnetic susceptibility(B.M.)	molar conductivity	hypredization	Proposed structure
[ZnL $(H_2O)_2$]	diamagnetic	5.1	Sp^3d^2	octahedral
[CdL $(H_2O)_2$]	diamagnetic	5.0	Sp^3d^2	octahedral
[HgL]	diamagnetic	5.1	Sp^3	tetrahedral

The Antibacterial Activity

The bacterial strain *Staph.Epidermidis* and *Enterobacter. spp* were used in this work and then cultured on muller-hinton medium and incubated at 37 ºC for 24 h the standardized antimicrobial disc were prepared from (H_2L, ZnL, CdL and HgL) by using sternal filter paper disc saturated with solution for each compounds [29], with conc. (100, 250, 500) ppm for each compound. For *Staph.Epidermidis* the highest inhibitory effect was observed in compound CdL fig- 11 ,then HgL , H_2L and ZnL respectively, For *Enterobacter. spp* the highest inhibitory effect was observed in compound HgL fig- 12 , followed by CdL and ZnL compound and then H_2L was low activity as show in table (4).

Table.4- Anti Bacterial Activity for Azo- Schiff Ligand and Complexes

bacteria	Staph.Epidermidis			Enterobacter. Spp		
Compound	100ppm	250ppm	500ppm	100ppm	250ppm	500ppm
H_2L_3	2	2	16	2	2	15
ZnL_3	2	2	10	2	10	10
CdL_3	30	35	40	2	10	12
HgL_3	8	12	25	10	12	15

Fig. 11- inhibitory effect for CdL in Staph.Epidermidis Bacteria

Fig. 12- inhibitory effect for HgL in Enterobacter. spp bacteria

Conciusion

The preparation of New azo-Schiff ligand included two steps , first: diazotization reaction for P-phenoxy aniline with Salcyldehyde to prepare azo compound , and second step included condensation reaction between triethylenetetraamine and azo compound to prepare ligand, all prepared compounds were colored , insoluble in water and stable towards temperature and air., the spectroscopic data ,FT-IR, UV-Vis and ^{1}H-NMR , C.H.N. , Atomic absorption as well as magnetic the success stability Suggested octahedral geometry around the Cadmium , Zinc ions and tetrahedral geometry around Mercury ion. molar conductivity show that all complexes were non- electrolytic. in addition antibacterial activity show highest inhibitory effect was observed in compound CdL with Staph.Epidermidis Bacteria and in compound HgL with Enterobacter. spp bacteria.

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