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Synthesis and study of Hg (II) complex with ligand derived from 4,5-diphenyl imidazole

Muntadher M.AL-Kishwan
University of Karbala-College of Education for Pure Science-Chemistry Dept.
Corresponding author email: muntadher.mohammed@s.uokerbala.edu.iq

Muneer A. AL -Da،amy
University of Karbala-College of Education for Pure Science-Chemistry Dept.

Salih H. Kadhim
University of Babylon-College of Science-Chemistry Dept.

***Abstract*---**A simple, rapid, sensitive and accurate spectrophotometric-method has been developed for the determination of Mercury (II).using the azo-Schiff reagent 1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl)methyl)phenyl)-N-(4-nitrobenzyl)ethan-1-imine(DMIPNI) react with Mercury (II) solution in the pH= 7 and to form Red complex. The complex shows λ_{max} at 517 nm with a malar absorptivity 2.44×10^5 L.mo1^{-1}.cm^{-1} and Sandell's sensitivity 8.2184×10^{-4} µg.cm^{-2} .Beer's law is obeyed in the concentration range (0.1 – 2 µg.mL^{-1}) of Hg (II) with an extremely high degree of linearity as indicated by the correlation coefficient value of 0.9994 with detection limit of 0.0119 µg.ml^{-1} and The limit of quantification is 0.0398 µg.ml^{-1}. The nature of complex showed that (M:L) ratio was 1:2 The stability constant of the complex was 2.7368×10^9 mol.L^{-1} , This spectrophotometric method is considered to be highly sensitive using a detector (DMIPNI).

***Keywords*---**azo-Schiff, Mercury (II), Spectrophotometric, Imidazole.

Introduction

Mercury is a powerfully poisonous element that affects human and public health as well as the environment, however the threat from mercury to humans and wildlife at high levels is mainly caused by the intake of water and food polluted with mercury. [1,2], The majority of mercury pollution is caused by human activities, however another source exists in the atmosphere and reaches ecosystems via atmospheric deposition. Mercury oxidizing compounds exert a more localized impact than pure mercury. [3], Mercury (Hg) experiences a number of complicated transitions and cycles between the interrelated atmospheric, oceanic, and Earth systems in the natural world. While metallic mercury (Hg^0) is a

liquid, it rapidly transforms into a hazardous vapor. Mercury's propensity to make chemical bonds with other elements (such as chlorine, sulfur, or oxygen) results in the development of inorganic mercury (Hg^{1+}) and mercury salts (Hg^{2+}), and bacterial activity can convert inorganic mercury to organic mercury. Important organic form of mercury in terms of toxicity is methyl mercury. Humans are exposed to mercury largely through water and food, with fish and shellfish consumption being the primary source. [4-7], Which allows the researcher to estimate the trace concentrations of mercury ion in water samples and analytical models in such a way that the spectral measurement utilizing reagents (DMIPNI) are regarded as vehicles azo imidazole component is crucial to the automobile manufacturing process. Azo-schiff a large number of other vehicles that were used in research and technology, and the results obtained from these compounds have tremendous value in life [8], and of importance in the diagnosis of organic used as reagents in measuring optical density [9], and in analytical chemistry referred to as spectral reagents [10], so they are characterized by high stability fast with metal ions and interaction, as well as sensitivity and high selectivity [11], which facilitates the selec-tion of the target.

Experimental

Materials

Without any further purification steps, the solvents & chemical-reagents utilized in this investigation were provided by “B.D.H, Fluka, and Merck”.

Instrumentation

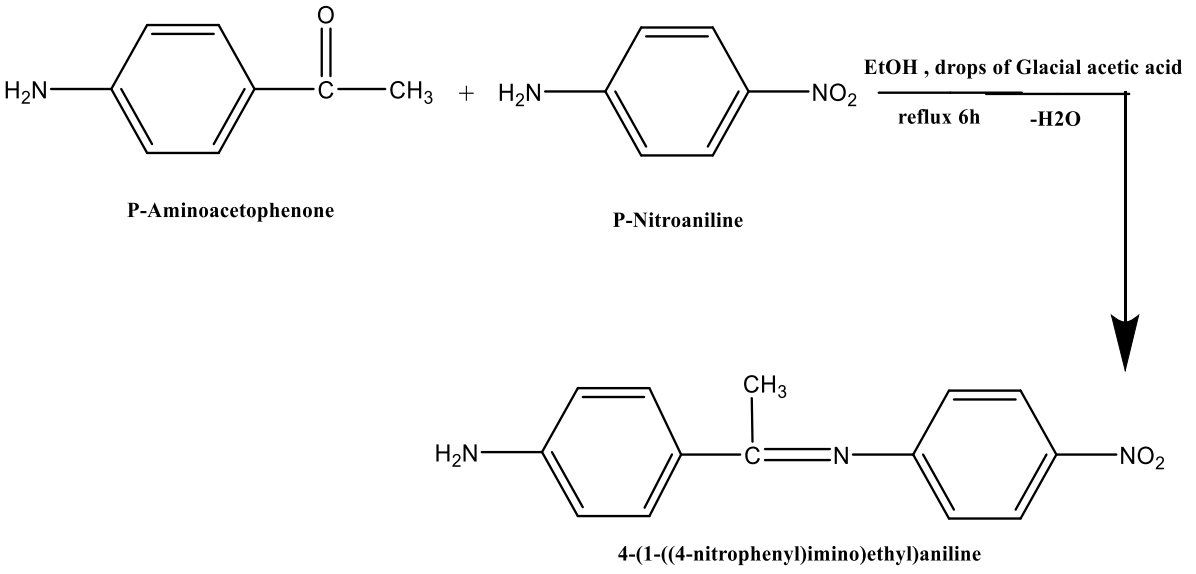
All approaches that were used in characteristic investigation of the produced ligand and its complexes were a -UV-6100 PC Double beam Spectrophotometer (EMCLAB ,Germany), FT-IR Spectrometer, Bruker Tensor II in range 500-4000cm',Germany, pH-meter (InoLab, WTW, 135i, Germany); Conductivity meter (Digital, InoLab, Germany); Melting point (SMP 30,Stuart,England); Balance BL 2105 (Sartorius,Germany): Mova 400 MHZ, 1HNMR, ^{13}CNMR spectrophotometer .

Procedure

Synthesis of new ligand(DMIPNI)

The ligand “1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl)methyl)phenyl)-N-(4-nitrobenzyl)ethan-1-imine(DMIPNI)” , as shown in scheme l . below

The first step

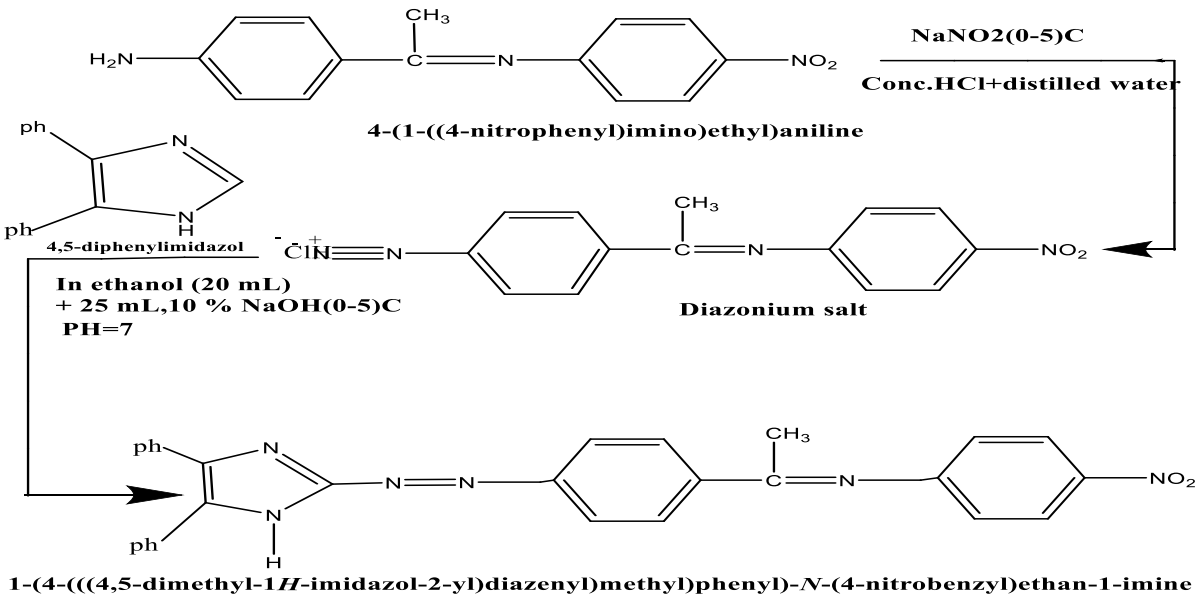


P-Aminoacetophenone

P-Nitroaniline

4-(1-((4-nitrophenyl)imino)ethyl)aniline

The second step



4-(1-((4-nitrophenyl)imino)ethyl)aniline

4,5-diphenylimidazol

Diazonium salt

1-(4-(((4,5-dimethyl-1*H*-imidazol-2-yl)diazenyl)methyl)phenyl)-*N*-(4-nitrobenzyl)ethan-1-imine

(DMIPNI)

Scheme 1 . Pathway of synthesis of ligand "1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl)methyl)phenyl)-N-(4-nitrobenzyl) ethan-1-imine(DMIPNI)"

Preparation of the divalent Mercury (II) compound

The "Mercury complex" was prepared $HgCl_2$ in 10 mL of buffer solution in pH=7. and (2 mmol) in 20 mL of ethanol absolute of ligand , the mixture solution of metal ligand was heated at (50-60) °C for 1h, the precipitate was washed and recrystallized the molar ratio (1:2) (M:L) by dissolving (1mmol) of the "Mercury(II) chloride salt" with "ethanol absolute" and dried in air. Table 1 show the physical properties of ligand and its complex .

Table 1: physical properties of (DMIPNI) and (Hg-DMIPNI).

No.	Molecular -formula	Color	m.p. (°C)	Yield (%)	Reaction Time.(h)
1	$C_{29}H_{22}N_6O_2$	Reddish Brown	135-137	79.92	5
2	$[Hg(C_{29}H_{22}N_6O_2)_2Cl_2$	Red	180-182	81.26	1

Results & Discussion

"UV-Visible Spectrophotometry" "UV-Vis spectrum" of the solid "Mercury complex solution" dissolved in ethanol showed the appearance of absorption peaks. It is observed that there is a clear difference in the (λ_{max}) values of the ligand "(DMIPNI)" and the complex "(Hg-DMIPNI)" formed with a red shift towards a higher wavelength . as shown in Figure 1 and Table 2.

Table 2: The "electronic transitions" of (DMIPNI) ligand and complex (Hg-DMIPNI).

Molecular -formula	λmax (nm)	Wave number(cm^{-1})	type of Transition
$C_{29}H_{22}N_6O_2$	470	21276	n→π*
	301	33222	π→π*
$[Hg(C_{29}H_{22}N_6O_2)_2Cl_2$	517	19342	CT
	294	34013	π→π*
	203	49261	π→π*

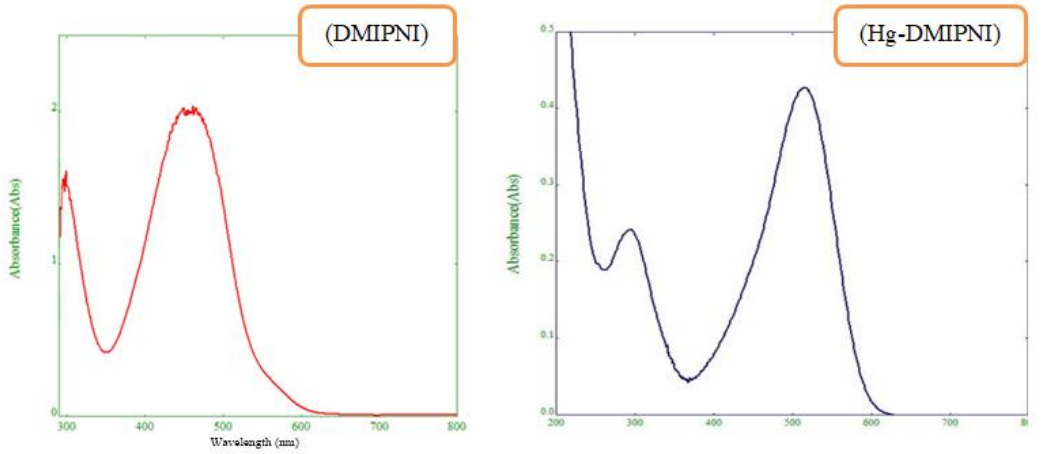


Figure 1: The "UV-Vis spectrum" of ligand(DMIPNI) and complex(Hg-DMIPNI).

Optimal Conditions Study for the Formation of the (Hg-DMIPNI).complex

pH effect

A group of 10 ml vials were filled with 1 ml of mercury ion solution at a concentration of (1×10^{-4} M) and the remaining volume was filled with a buffer solution with a pH value ranging from 5 to 11 to yield a concentration of (1×10^{-5} M). The ligand solution was generated by removing 1 ml from the ligand solution (1×10^{-4} M) and adding 100% ethyl alcohol to get the desired concentration (1×10^{-5} M). Then, by combining 1ml of the mercury ion with 1ml of the ligand and increasing the acid function to the extent of the mercury's absorption record at its highest wavelength, we observe an increase in absorbance values at pH=7, followed by a fall due to the formation of unstable complexes. Ions of mercury[12], as depicted in Figure 2.

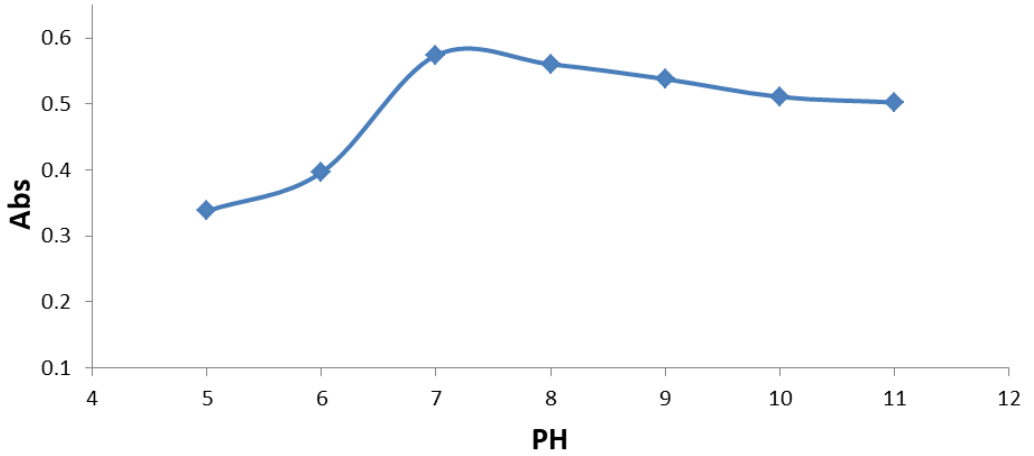


Figure 2: Effect of PH value in complex (Hg-DMIPNI).

Ligand concentration effect

A series of solutions were made by combining (1×10^{-5} M)Mercury(II) ion solution with various concentrations of ligand (DMIPNI) ranging from (0.5×10^{-5}-4×10^{-5} M), the acidic function was set to pH=7, and the absorbance was measured against water and ethanol as a blank solution. Figure 3 depicts the effect of ligand (DMIPNI) concentration on the results, which reveal that the best ligand concentration was (3×10^{-5} M).

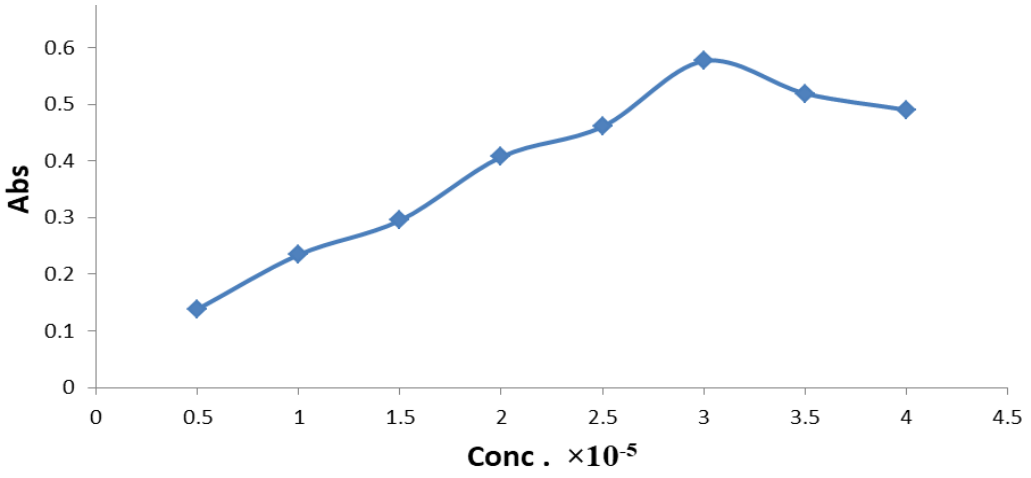


Figure 3: effect of ligand concentration

Effect of time in stability of (Hg-DMIPNI) complex

The interaction of the ligand with mercury was monitored over a period of time ranging from (2-120 minutes). To determine the stability of the formed compound, we note that the reaction was completed immediately when adding the reagent solution to the mercury solution, which indicates that the mercury complex has high stability and stability[13], in the mercury solution with the ligand (DMIPNI), as shown in the figure.4

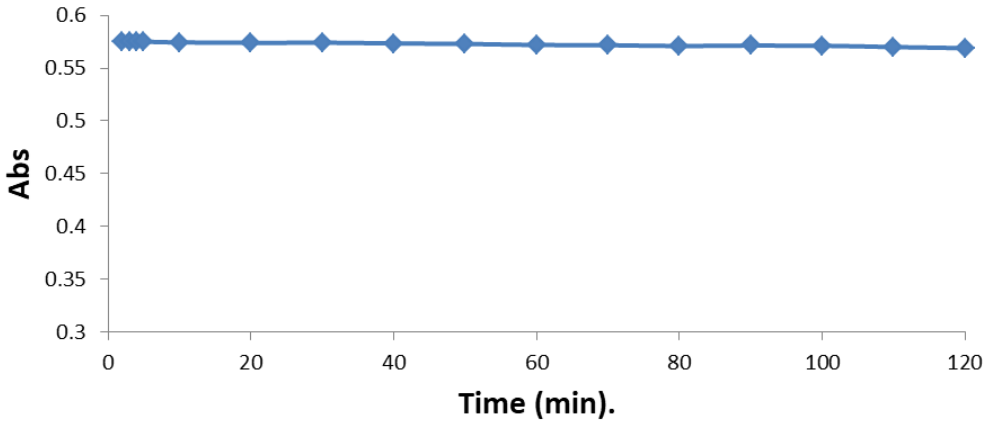


Figure 4: Effect of time in stability of (Hg-DMIPNI).

Effect of Temperature in stability of (Hg-DMIPNI)complex

Figure 5 demonstrates that the mercury complex's absorption values reach their maximum and provide the greatest color intensity between 10 and 25 degrees Celsius, and subsequently drop with increasing temperature. This is due to the mercury complex's limited stability or its dissociation at high temperatures.

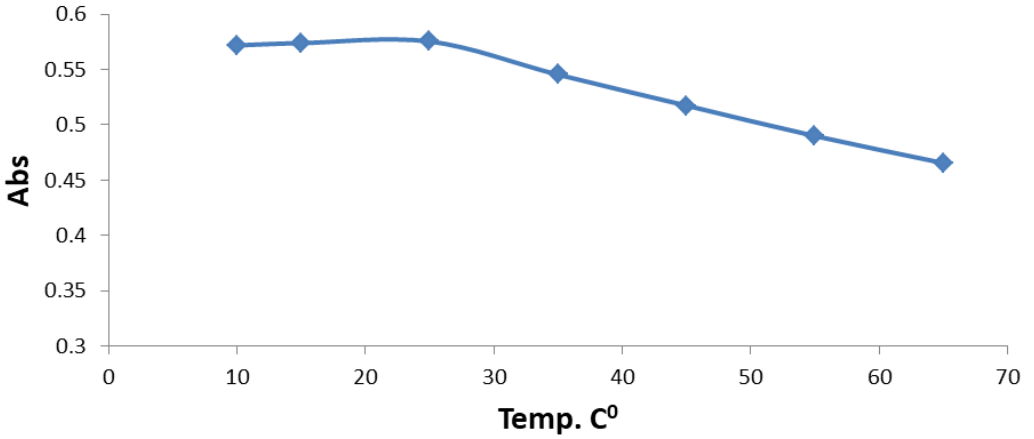


Figure 5: Effect of Temperature in stability of (Hg-DMIPNI)complex .

Effect of the order of addition in the composition of the (Hg-DMIPNI)complex

Addition sequences have an effect to investigate the effect of addition sequences under ideal conditions, the method outlined in Table (3) was used.

Table 3: Effect of the order of addition in the composition of the (Hg-DMIPNI)complex

Sequence of addition number	Sequence of addition	Abs (Hg-DMIPNI)
1	M + L + pH	0.5725
2	L + M + pH	0.5670
3	M + pH + L	0.5602
4	L + pH + M	0.5515

The addition of the first degree was chosen based on the highest absorption attained, as shown in Table (3).

Study the construction of calibration curve of (Hg-DMIPNI)complex

Study the construction of the calibration curve. The mercury compound with the ligand obeys the Beer-Lambert Law in the range (0.1-2.0 µg/ml) as shown in Figure 6, with a high molar absorption coefficient. This method has a high sensitivity and can be used for determination of mercury at very low concentrations.

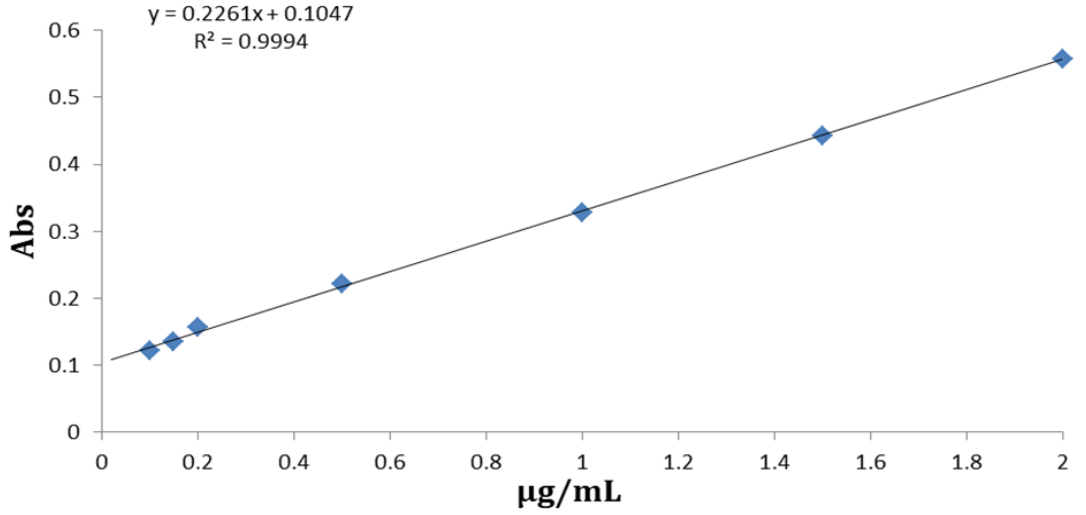


Figure 6: Calibration curve of (Hg-DMIPNI)complex

Table 4: construction of calibration curve of (Hg-DMIPNI)complex.

(Hg-DMIPNI) Conc. µg/mL	Regression Equation	Slope	ε (L.mol^{-1}.cm^{-1})	R^2	S (µg.cm^{-2})	L.O.D ppm	L.O.Q ppm
0.1-2.0	0.2261x+0.1047	0.2261	2.44×10^5	0.9994	8.2184×10^{-4}	0.0119	0.0398

Study the stoichiometry of the composition of complex

The stoichiometric of the cadmium complex was found using two methods :

Method of proportionality

A constant and known concentration of cadmium ion was utilized with varying concentrations of ligand (0.5×10^{-5}- 4×10^{-5} M) to determine the metal ion to ligand ratio, and the study results revealed that the ratio is (1: 2) (M : L), as shown in Figure 7.

Job Method (continues changes)

To find the ratio of the metal ion to the ligand, use several sizes of the metal ion (0.5- 4 mL) and varied sizes of the ligand (0.5-4 mL) and find that the ratio is (1:2)(M:L)as indicates Fig 7.

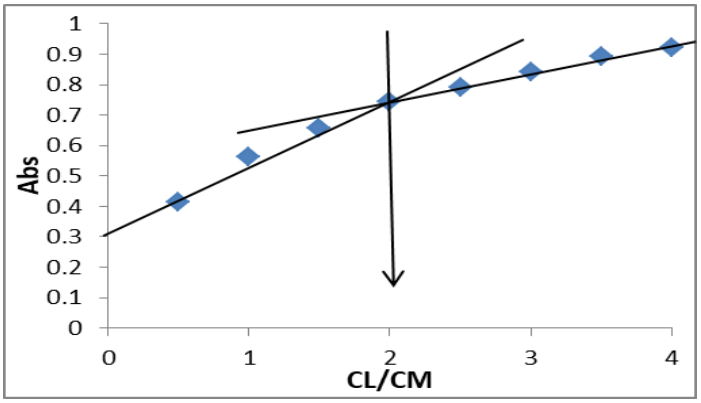


Figure 7: Molar ratio methods of (Hg-DMIPNI)

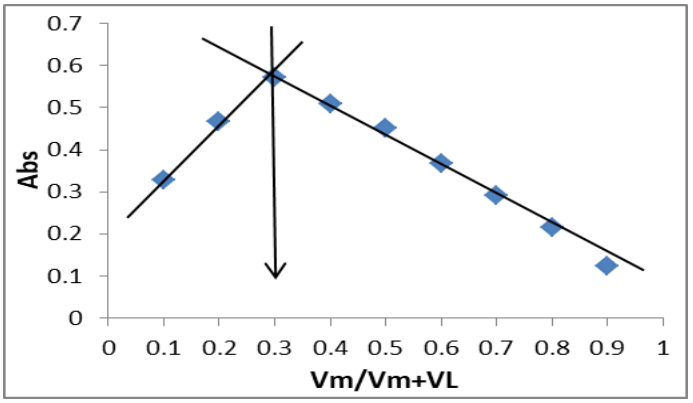


Figure 8: Continuous variation method of (Hg-DMIPNI)

Study the stability calculation of the (Hg-DMIPNI)complex

Table 5: shows the absorption values (As) and (Am) of the mercury complex, as well as the values of each (α), (K st), and (Kinst).

The determination metal ion	As Value	Am Value	α	Kst mol.L^{-1}	Kinst L.mol^{-1}	Log Kst
Hg (II)	0.7430	0.9225	0.1945	2.7368 ×10^{9}	3.6538×10-10	9.4372

From the results of molar ratios show the stability of the mercury complex by calculating the degree of dissociation and stability of constant .

Study the determination of "thermodynamic function" to complexes formation

"Thermodynamic function ΔH^0 ,ΔG^0 and ΔS^0" were calculated, results were illustrated in table 6 and figure 9.

Table 6: The effect of temperature on thermodynamic function for (Hg-DMIPNI) complex.

T (K)	1/T K^{-1}	Log K_{st}	-ΔH (K. J/mole)	-ΔG (K.J /mole)	-ΔS (K.J /mole . K)
288	0.0034	9.6462		53.1835	0.1846
298	0.0033	9.5983		54.7569	0.1837
308	0.0032	9.5565	0.0079	56.3477	0.1829
318	0.0031	9.5101		57.8950	0.1820
328	0.0030	9.4700		59.4635	0.1813
338	0.0029	9.4293		61.0131	0.1805

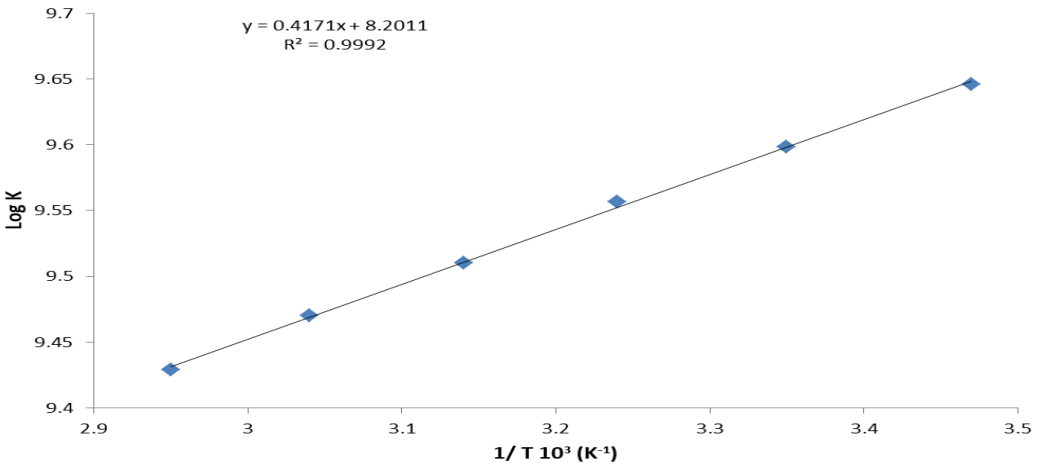


Figure 9: Relationship of Log Kst and 1/T of (Hg-DMIPNI) complex

As demonstrated by the negative enthalpy value, the reaction was exothermic. It's worth noting that as the temperature drops, the likelihood of complex creation rises. Furthermore, as demonstrated by the negative sign [14], the reaction occurred spontaneously. The complex's stability is confirmed because the entropy value approaches zero (less random and spontaneous).

Precision

To determine the precision of the analytical technique, The quantity of "standard deviation (S.D)" and "relative standard deviation (percent R.S.D)" for the difficult and ideal conditions[15], were calculated in table 7.

Table 7: Values of standard deviation, percentage standard deviation.

Comp. of ion	Conc. Of ion (µg/mL)	S.D	R.S.D%
Hg (II)	0.1	0.0010	0.3716
	0.5	0.0014	0.4195
	1.5	0.0008	0.1623

Accuracy

Accuracy The term "accuracy" refers to the precision and accuracy achieved by closely approximating the real value to the theoretical value. The analytical method's accuracy[16], is calculated using the percentage relative error and the pre-processing ratio of previously created complexes, as shown in table 8. The results reveal that the cadmium estimation method using ligand (DMIPNI) is extremely accurate.

Table 8: The relative percentage error and the pre-processing ratio of ligand complex.

Complex ion	Analytical value (µg/mL)	d	E_{real} %	Re %
(Hg-DMIPNI)	0.1	-0.0014	-1.4	98.6
	0.5	0.1570	3.14	103.14
	1.5	-0.0051	-0.34	99.66

Study of "FT-IR spectra" for ligand and complex

Figures 10 and Table 9 explained the "FT-IR" study and the absorption frequencies for ligand and the (Hg-DMIPNI) complex [17] .

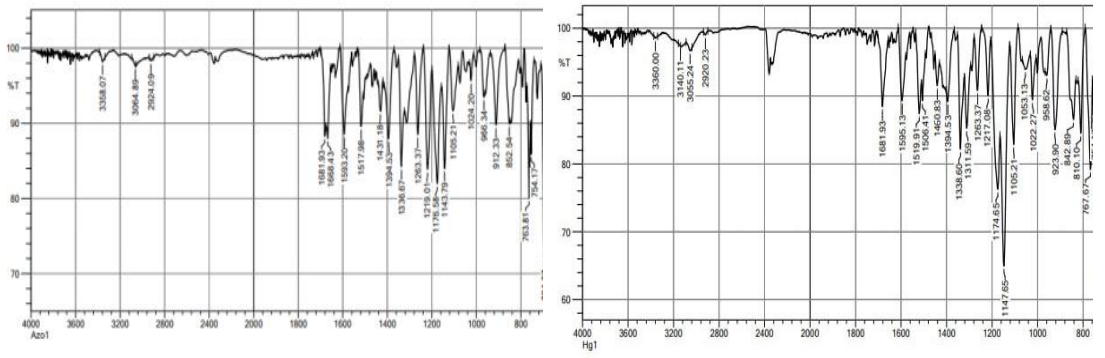


Figure 10: **"**FT-IR spectrum" of ligand (DMIPNI) and (Hg-DMIPNI) complex.

Table 9: Typical FT-IR absorption frequencies for ligand and complexes.

Compound	V N-H	V N=N	V C=O	V Ph.imid	M-N
Ligand-DMIPNI	3358 (w)	1431 (w)	1668 (m)	763 (s)	----
Hg-Complex	3360 (w)	1460 (w)	1681 (m)	767 (s)	459(m)

Magnetic Resonance Spectrometer

^{1}H NMR Spectra of ligand (DMIPNI)

The ^{1}H NMR Spectra of ligand shows the chemical displacements of aromatic and elliptical protons, the single bond at (8.47 ppm) belong to one proton of amine group (NH) in imidazole cyclic , the bonds at (6.03-8.2ppm) belongs to (H-Ar) , (2.67 ppm) due to the proton of (CH3) , while the band at (2.5 ppm) related to (DMSO d^6) [18.19] , and pack at (3.36 ppm) an indication of moisture as in figure 11.

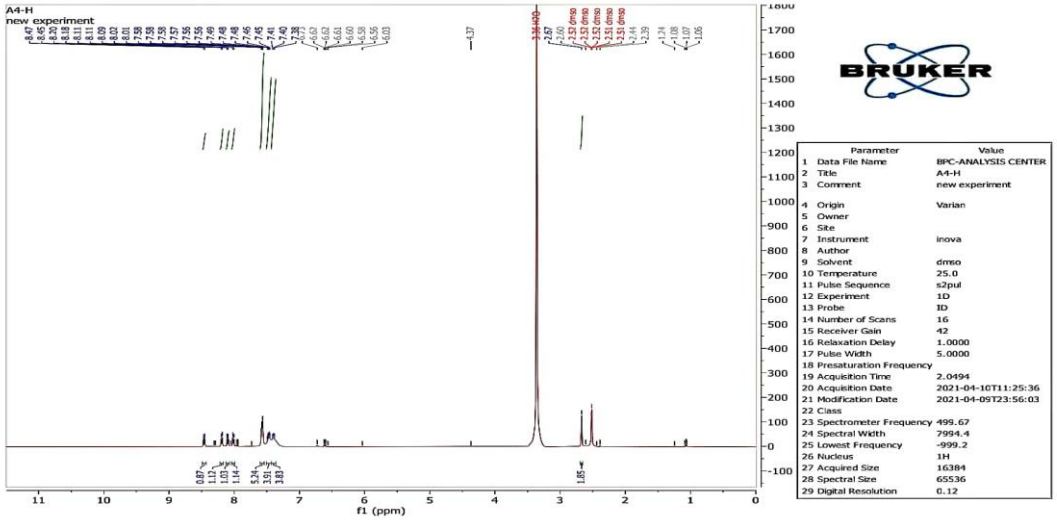


Figure 11: ^{1}H NMR spectra of ligand (DMIPNI).

^{1}H NMR Spectra of complex (Hg-DMIPNI)

The ^{1}H NMR Spectra of ligand shows the chemical displacements of aromatic and elliptical protons, the single bond at (8.31 ppm) belong to one proton of amine group (NH) in imidazole cyclic , The aromatic ring protons in displacement (6.58 -7.95 ppm), (2.60 ppm) due to the proton of (CH_3) ,while the band at (2.50 ppm) related to (DMSO d^6) [18,19] , and pack at (3.35 ppm) an indication of moisture , as in figure 12

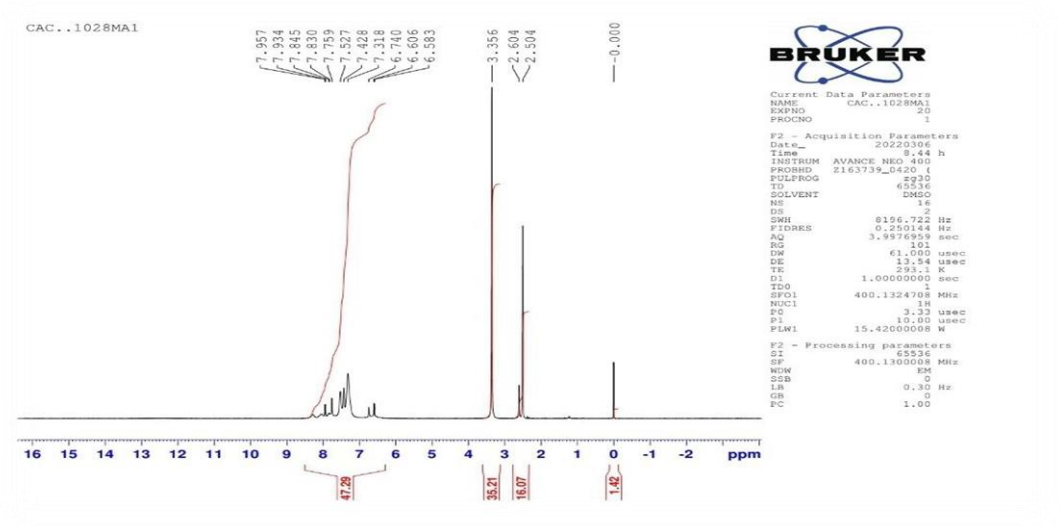


Figure 12: ^{1}H NMR Spectra of complex (Hg-DMIPNI)

Molar Electrical Conductivity of Complexes

In order to determine whether negative ions were present inside the coordination ball (non-electrolyte) or outside the coordination ball, the electrical conductivity of the produced complex was investigated at laboratory temperature and concentration (1×10-3). (electrolyte). It was discovered that the mercury complex behaves like non-electrolytic substances[20].

Table 10: Molar Electrical Conductivity of Complexes

Molecular formula	Molar electrical conductivity ($Ohm^{-1}.mol^{-1}.cm^{2}$)
	Ethanol
$[Hg(C_{29}H_{22}N_6O_2)_2Cl_2]$	15.3

Magnetic Sensitivity Measurements

One of the straightforward and crucial methods for identifying and understanding transition metal complexes is magnetic sensitivity studies. The findings of magnetic sensitivity demonstrated that the mercury complex had octahedral geometries and magnetic diamagnetic properties of the ligand[21], as given in the table (11).

Table 11: Magnetic Sensitivity Measurements

Metal complex	Hg(II)complex
Xg	0
X M	0
D	-0.00062176
XA	0.00062176
µeff	1.2070
T(K)	20+273=293

Suggested Structure of the Complex

A suggestion of the complex structure, as shown in Figure 13, is due to FT-IR spectra, and the stoichiometry obtained from job, slope analysis and mole ratio methods.

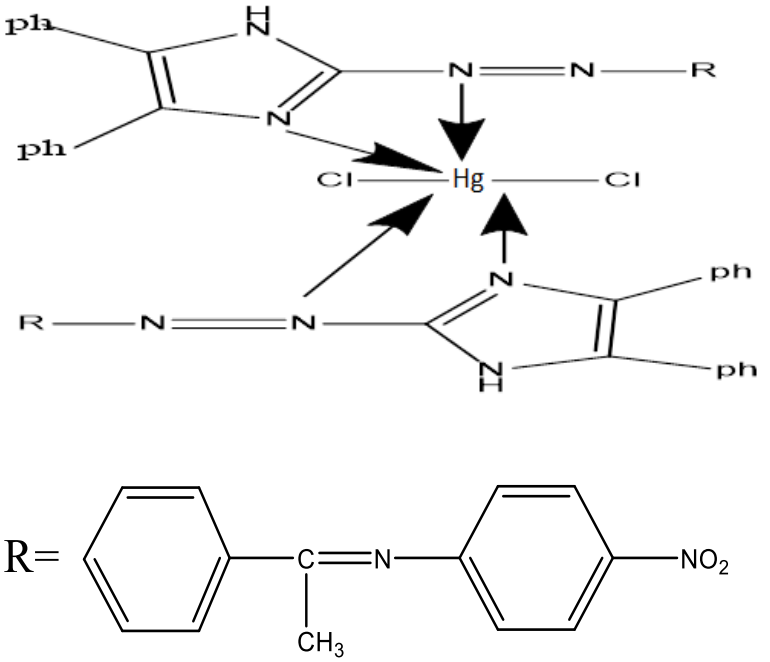


Figure 13: The suggested structures of "Mercury(II) Complex.

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