

Article

Synthesis, Characterization, Antimicrobial Activity of New Schiff Base Complexes and Thermodynamic Study for Adsorption of Pt(IV) Complex Using Bentonite

Mohammed I.M. Al-Nissani¹, Malath Khalaf Rasheed² and Lekaa K. Abdul Karem^{*3}.

^{1,2}Department of Chemistry, College of Education, Samarra University, Iraq

³Departments of Chemistry, College of Education for Pure Sciences, Ibn Al-Haitham, University of Baghdad, Iraq

¹For Corresponding author: Email address: mohamed_mahdi@uosamarra.edu.iq

^{3*}For Corresponding author: Email address: likaa.k.a@ihcoedu.uobaghdad.edu.iq

Abstract

New complexes were prepared by reacting metal ions Pt(IV), Hg(II) and Zn(II) with the Schiff base LH, (E)-3-hydroxy-4-((pyridin-3-ylmethylene)amino) naphthalene-1-sulfonic acid. The new Schiff base and the prepared complexes were characterized by using Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis), mass spectrometry and nuclear magnetic resonance spectroscopy (¹H-NMR). The new Schiff base acts as a bidentate ligand, coordinating with the metal ions through the nitrogen atom of the azomethine group and the deprotonated phenolic oxygen atom. Spectroscopic and analytical measurements revealed that the geometry of the Hg(II) and Zn(II) is tetrahedral geometry and for the pt(II) is octahedral. The ligand and its complexes were tested for their antimicrobial activities, and the isothermal adsorption of the platinum complex was studied.

Keywords: Adsorption, Bentonite, Conductivity, Thermodynamic, Schiff base complexes, Sulfonic acid, 3-pyridinecarboxaldehyde

Introduction

The term Schiff base was initially used to refer to organic compounds containing the active group (-C=N-). These compounds were first synthesized by the German chemist Hugo Schiff in 1864 through a simple condensation reaction between aldehydes or ketones and primary amines ^(1,2). Schiff bases hydrolyze rapidly in acidic aqueous media but remain stable in basic media ⁽³⁾. Many Schiff bases are used as chelating ligands, with the bidentate ligand being widely used in

the preparation of metal complexes. These ligands are classified according to the donating group into N, N-donating and N,O-donating groups^(4,5). Schiff bases are known by various names including imines, anils, azomethines, benzanils, ketimines⁽⁶⁾, which come from ktonat also known as aldimines if they come from aldehydes^(7,8). metals Hg(II), pt(II) and Zn(II) Complexes have been created with the use of 3-hydroxy-4-[N-(2-hydroxynaphthylidene)-amino]-naphthalene-1-sulfonic acid Schiff base as a ligand produced by the condensation process of 4-amino-3-hydroxynaphthalene-1-sulfonic acid and 2-hydroxy-1-naphthaldehyde⁽⁹⁾. The DFT approach was done on 4-amino-3-hydroxy naphthalene-1-sulfonic acid (ANSA). Different spectroscopic analyses like NMR, FT-IR, and UV-Visible were performed⁽¹⁰⁾. In particular, a new Schiff base was synthesized from the reaction of (4-amino-3-hydroxynaphthalene-1-sulfonic acid) with (3-pyridincarbalddehyde) to form a new Schiff base, which was used as a bidentate ligand. The newly synthesized Schiff base was characterized spectroscopic and its biological activity as well as the isothermal adsorption of the platinum complex were studied.

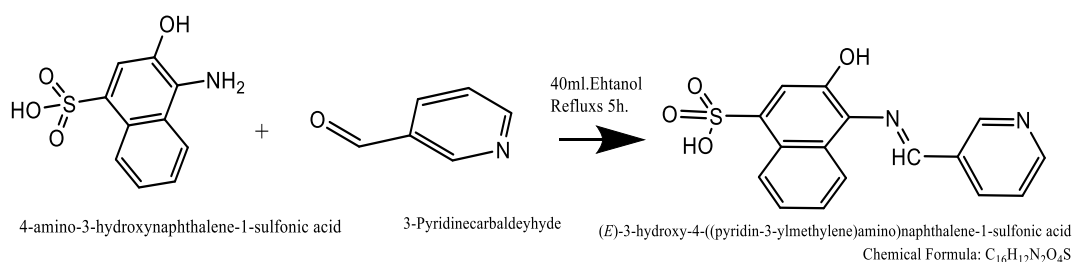
Materials and Physical measurements

The laboratory materials used were of high purity and did not require additional purification. They were purchased from excellent sources. The melting points of the ligands and prepared complexes were measured using a Melting Point Advanced SMP30 electrothermal melting point apparatus from Stuart United Kingdom. Infrared spectra of the ligands and their complexes were recorded using a Shimadzu FT-IR-8400 spectrometer in the range of 4000 – 400 cm⁻¹, with samples prepared as KBr discs. UV-Visible spectra of the ligands and their complexes were recorded using a Shimadzu UV-160A spectrometer. ¹H-NMR spectra of the ligands dissolved in DMSO-d₆ were recorded using a 300 MHz ultra-shield model NMR instrument, with tetramethylsilane used as an internal reference. The metal content in the prepared solid complexes was determined using atomic absorption spectroscopy with a Shimadzu Atomic Absorption / Flame Emission spectrophotometer (A.A-160). Mass spectra of the ligands and complexes were recorded using a Shimadzu GCMS-QP2010SE spectrometer. The required weights of the ligands, metal ion salts, and other substances were measured using a RADWAG WAGI ELEKTRONICZNE AS220-X electronic balance. Reflux heating was performed using an IKA RHB2 reflux heater. The culture medium was sterilized using autoclaving at 120°C and 1.5 pressure. The percentage of carbon, nitrogen, and hydrogen (CHN) in all complexes was measured using a Euro EA 3000 analyzer.

Preparation of Schiff base ligand L₁ and its Complexes

The ligand was prepared by adding (2 mL, 0.0209 mole) of 3-Pyridinecarbalddehyhyde in (10 mL) of absolute ethanol in a round-bottom flask of (100mL). Then, with a gradual adding and continuous stirring of (5.00 g , 0.0209 mole) of 1-amino-2-naphthol-4-sulfonic acid, that was eliminated in 30 ml of absolute

ethanol. The concoction was left in light of reflux for 4 hours at 80°C. Subsequently, the reaction flask was placed in an ice bath for several minutes, then the precipitate was filtered and left to dry, resulting in a green precipitate weighing 4.7 g with a yield of 62% and a melting point of 254°C, as shown in the following reaction equation. The complex was prepared by dissolving 0.3 g (0.000914 mole) of ligand (L1) in 10 ml of absolute ethanol. Then, 0.036 g of sodium hydroxide (NaOH) dissolved in 10 ml of absolute ethanol was added to the solution. Then, the mixture was gradually added to metal chlorides (Hg(II), Zn(II),) and evaporated in 10 ml of ethanol with continuous stirring in a 100 ml round-bottom flask. The mixture was refluxed for 4 hours at 80°C. After that, the solution was filtered after cooling it in an ice bath, and then dried, and the weight of the precipitate was measured, along with its melting point. The Platinum is prepared in a different way. The Platinum chloride is melted in distilled water in a (100 ml) round-bottom flask and with a continuous stirring for fifteen minutes. During this time, 0.3 g (0.000914 mole) of Schiff base ligand is melted in (10ml) of absolute ethanol. Then 0.04 g of (KOH) which is also melted in (10ml) of absolute ethanol, was added to the ligand. This solution was added to the Platinum chloride which was melted in the distilled water and left for stirring. The mixture was left to reflux for 4 hours. Then the solution was filtered after cooling it in an ice bath, and then dried, and the weight of the precipitated was measured along with its melting point.



Scheme 1: The Preparation of the Schiff base ligand (L₁)

Antimicrobial activity

The prepared compounds were tested against various bacteria and fungi using petri dishes⁽⁹⁾⁽¹⁰⁾. This test includes two types of bacterial isolates, one being Gram-negative (Gr-ve) *Escherichia coli* and the other being Gram-positive (Gr+ve) *Staphylococcus aureus*, and a type of fungus, *Candida albicans*, was also included in the test. Specific weights of the samples were dissolved in the solvent (DMSO) to create three different concentrations for each: (75 mg, 50 mg, and 25 mg). Then, 40 µL of the antibiotic neomycin sulfate at a concentration of 75 mg was added for bacterial testing, and 40 µl of the standard antifungal agent *Nystatin* at a concentration of 75 mg was added for fungal testing. The antibiotics served as a control group. The petri dishes were then incubated at 37°C for 24 hours for bacterial strains and at 31-32°C for 48 hours for the

fungus strain. The antimicrobial activity of each microorganism was evaluated by measuring the diameter of microbial growth inhibition (in millimeters).

Adsorption of Complex Using Bentonite

The spectrum used in this study was acquired by the Geological Survey General Company, where this spectrum is found in the Western Desert (Al-Anbar). It has a yellow color and a smooth texture, does not dissolve in organic and inorganic acids, as well as in hydroxyl compounds. The bentonite surface was prepared by washing the bentonite clay with deionized ion-exchanged water several times (more than ten times) to remove any suspended materials and salts present in the clay. After that, the clay was dried using a laboratory oven at 100 degrees Celsius for six hours until completely dried. Then, the clay was grinded using an electric grinder, followed by sieving through a sieve with a particle size of 75 μm (sieve $\leq 75 \mu\text{m}$), equivalent to 200 mesh. A standard solution for the platinum (II) complex was ready through the dissolution 0.01g of the complex in 3ml of ethanol and transferring it to a volumetric flask with a capacity of 250ml. The volume was then completed to the mark using ethanol solvent, resulting in a standard solution concentration of 100 ppm. To determine the calibration curve for the platinum complex, a series of diluted solutions were prepared with concentrations ranging from 5 to 50 ppm. The absorbance of these solutions was measured at $\lambda_{\text{max}}=475 \text{ nm}$, and by drawing the absorbance values against the concentration values and applying the Beer-Lambert law, the calibration curve depicted in Figure (1) was obtained.

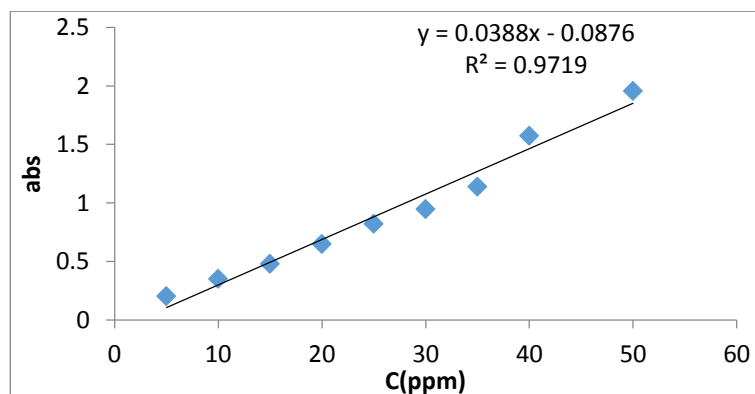


Figure 1: Calibration Curve of platinum complex

To determine the equilibrium time between the montmorillonite clay surface and the platinum complex, the factors (the weight of the adsorbent surface, solution volume, cobalt complex concentration, and temperature) were kept constant, with only time being the variable factor. A volume of (10 ml) of the complex solution at a specific concentration was added to volumetric flasks containing the weight of the adsorbent surface used in this study. These volumetric flasks were placed in a water bath shaker at a temperature of 25 degrees Celsius,

additionally a speed of (150 rpm). After the shaking time for each volumetric flask, the separation process was conducted using a centrifuge at a speed of (4000 rpm) for (5 minutes). Subsequently, the filtration process was carried out, and the supernatant was collected. The absorbance of the supernatant was calculated using UV-visible spectrophotometry at λ_{max} for the platinum complex. The concentration at time t , C_t (mg/L), was measured using Equation (1) derived from the calibration curve where; A = Absorption; m = Slope; C_t = Concentration, b = Intercept. Then, the volume of material adsorbed material at time t , q_t (mg/g), was calculated using Formula (2), where; q_t = Amount of adsorbed material at time t (mg/g); C_0 = Initial concentration of the adsorbed solution (mg/L); V_{sol} = Total volume of the adsorbed solution (cobalt complex) (L); C_t = Concentration at time t (mg/L); W = Weight of the adsorption surface (g)⁽¹¹⁾

$$A = mc_t + b \dots (1) \quad \text{and} \quad q_t = \frac{V_{\text{sol}}(C_0 - C_t)}{W} \dots \dots \dots (2)$$

This process was repeated at other temperatures (35-45)°C. By monitoring the absorbance values over time, the equilibrium time was determined. To determine and define the adsorption of the isotherms, 10 ml of the complex solution at different concentrations were added to volumetric flasks containing the montmorillonite clay surface. This volumetric water bath shaker was filled with flasks at a pace of 150 rpm and at different temperatures (25-35-45)°C, based on the previously determined equilibrium time. After reaching equilibrium, the supernatant was separated from the precipitate using a centrifuge at 4000 rpm for 5 min. Then, filtration was carried out, and the absorbance of these samples was measured using UV-Vis spectrophotometry. The equilibrium concentrations (C_e) for each model were determined by referring to the calibration curve equation.

The percentage removal ($R\%$) was calculated using the following equation:

$$R\% = \frac{C - C_e}{C} \times 100 \dots \dots \dots (3)$$

Results and Discussion

The physical properties of the Schiff base ligand and its complexes

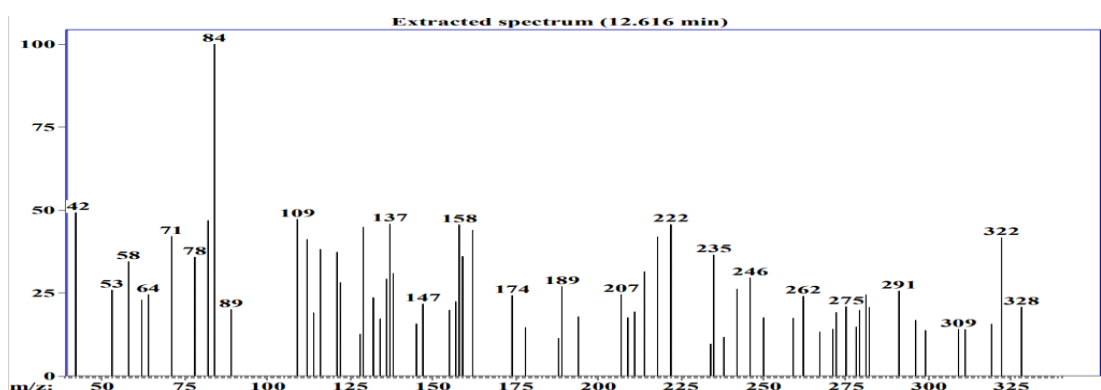
Some physical properties of the prepared Schiff base ligand and its complexes have been determined, such as color, molecular weight, and melting point. Elemental analysis (C.H.N) and atomic absorption spectroscopy have also been conducted, as shown in Table 1.

Table 1: physical properties of the Schiff base ligand and its complexes.

Compound Molecular Formula	Yield%	m.p °C	colors	(M.wt) (g/mol)	practical (Theoretical)%				
					C%	H%	%N	%S	%M
L₁ C₁₆H₁₂N₂O₄S	78	254	green	328.34	58.33 (58.32)	3.58 (3.51)	8.33 (8.36)	9.56 (9.58)	---
[Pt(L₁)₂Cl₂] C₃₂H₂₂Cl₂N₄O₈PtS₂	60	<300	Plack	851.59	43.42 (42.98)	2.51 (2.41)	6.33 (7.00)	7.24 (7.23)	22.90 (23.02)
[Hg(L₁)₂] C₃₂H₂₂N₄HgO₈S₂	64	<300	violet	855.26	44.94 (43.88)	2.59 (2.11)	6.55 (6.00)	7.50 (6.99)	23.45 (24.23)
[Zn(L₁)₂] C₃₂H₂₂ZnN₄O₈S₂	65	<300	lilac	720.05	53.38 (53.51)	3.08 (3.09)	7.78 (7.80)	8.90 (8.93)	9.07 (9.85)

Maas spectroscopy for ligand

The mass spectrum of the prepared ligand (L₁) showed a peak at $m/z=328$, corresponding to the formula (C₁₆H₁₂N₂O₄S). This peak shows how Molecular weight are ligand by determining the molecular ion significance of the prepared compounds and the base value ($m/z=328$). Additionally, the spectrum showed peaks corresponding to fragment ions generated from the cleavage of the molecule after ionization.

Figure 3: The mass spectrum of ligand (L₁)

¹H-NMR Spectrum of Ligand

The ¹H-NMR spectrum of ligand (L₁) in the ⁶DMSO-d₆ solvent Figure (4), which is deuterated at $\delta H=2.508$ ppm attributed to the protons of the solvent (DMSO). The spectra shows four signals at $\delta H=(8.92,10.13,8.97,11.12)$ ppm. The first signal corresponds to the proton of the sulfonic acid (OH) group. The second signal corresponds to the proton of the carbon atom attached to the nitrogen of the pyridine ring. The third signal corresponds to the proton of the phenolic (OH) group ⁽¹¹⁾. The fourth signal corresponds to the proton of the carbon atom of the azomethine (N=C-H) group. Two doublet signals at $\delta H=(8.72,8.792)$ ppm. A triplet signal at $\delta H=7.56$ ppm attributed to the protons of the pyridine ring. Two doublet signals at

$\delta H = (7.91, 7.60)$ ppm. Two triplet signals $\delta H = (7.42, 7.44)$ ppm, attributed to the protons of the second naphthalene ring⁽¹²⁾.

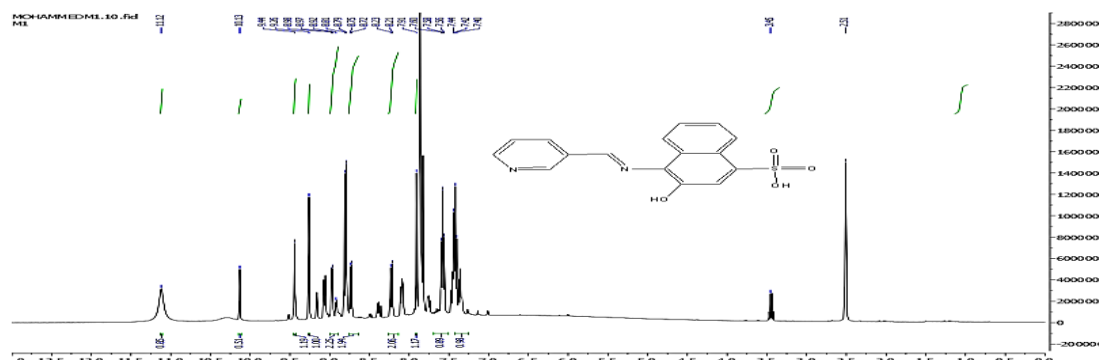


Figure 4: The ^1H -NMR Spectra of ligand (L_1)

FT-IR Spectra of the Schiff base and Complexes

The infrared spectrum exhibits absorption peaks at specific frequencies (659.68 cm^{-1}) corresponds to the (C-S) group, and another peak at (895.00 cm^{-1}) corresponds to (S-O)⁽¹²⁾. A strong peak observed at 1354 cm^{-1} is attributed to the (SO_2) group, and the peak at (1219 cm^{-1}) corresponds to (C-O) group. Additionally, the band at 1616.40 cm^{-1} is associated with the (C=N) group of the pyridine ring. The absorption peak for the (OH) group of sulfonic acid is observed at 2904.89 cm^{-1} , while the aromatic (C-H) observed at (3097 cm^{-1}). Furthermore, the (OH) peak of the naphthalene ring is evident at (3236.66 cm^{-1}). Notably, a significant peak related to the azomethine group⁽¹³⁾ (C=N) appears at 1639.55 cm^{-1} . The sulfonic acid (OH) peak is observed at (3413 cm^{-1}). Table 3, illustrates the main absorption peaks in the infrared spectra of Schiff base ligands and their complexes in units of (cm^{-1}). The IR spectra of the complexes exhibited new bands at $440\text{--}425\text{ cm}^{-1}$ and $501\text{--}505\text{ cm}^{-1}$ are assigned to ν (M-O) and ν (M-N) stretching frequency, respectively⁽¹⁴⁻¹⁶⁾, also indicating the coordination of the Schiff base ligand to the metal (II) ion.

Table 2: Infrared Spectra for Schiff Base Ligands and Their Metal Complexes

Compound	$\nu(\text{OH})$ phenol	$\nu(\text{C}=\text{C})$ aromatic	C=N Imine C=N ring	(C-H) aromatic	$\delta(\text{C}-\text{N})$	ν (M-N)	ν (M-O)
L_1	3414(m)	1531(s)	1639(m) 1616	3097(s)	1045(s)	---	---
$[\text{Pt}(\text{L}_1)_2\text{Cl}_2]$	---	1531(s)	1662 (m)	3097(s)	1049(s)	501 (w)	443(w)
$[\text{Hg}(\text{L}_1)_2]$	---	1531(s)	1660 (m)	3097(s)	1049(s)	503 (w)	440 (w)
$[\text{Zn}(\text{L}_1)_2]$	---	1531(s)	1658 (m)	3097(s)	1049(s)	505 (w)	445 (w)

s=strong, m=medium, w= weak

UV-Vis Spectroscopy for Ligand (LH)

UV-Visible spectrum of the prepared ligand (L₁) shows first intense absorption peak is observed at (280 nm) (35714 cm⁻¹), attributed to the electronic transition ($\pi \rightarrow \pi^*$)⁽¹⁷⁾. The second peak of moderate intensity appears at (350 nm) (28571 cm⁻¹), attributed to the electronic transition ($n \rightarrow \pi^*$). Table (3), illustrates the absorption band positions for the Schiff base ligand and its complexes⁽¹⁵⁾. The Pt(IV) complex show one absorption in d-d; the peak at 507 nm is due to $^1A_{1g} \rightarrow ^1T_{1g}$ that suggesting octahedral geometry of this complex. The Hg(II) and Zn (II) complexes show 419 nm attributed to charge Transfer (C.T) band, this is consistent with the tetrahedral shape of these complexes^(18,19).

Table 3: Absorption band positions for Schiff base ligand and its complexes.

Compounds	λ (nm)	ν (cm ⁻¹)	Transition	proposed geometric shape
[L ₁]	278	35971	$\pi \rightarrow \pi^*$	-----
	336	29761	$n \rightarrow \pi^*$	
[Pt(L ₁) ₂ Cl ₂]	281	35587	$\pi \rightarrow \pi^*$	Octahedral planar
	328	30487	$n \rightarrow \pi^*$	
	350	28571	C.T	
	507	19723	$^1A_{1g} \rightarrow ^1T_{1g}$	
[Hg(L ₁) ₂]	282	35460	$\pi \rightarrow \pi^*$	Tetrahedral planar
	419	23866	C.T	
[Zn(L ₁) ₂]	282	35335	$\pi \rightarrow \pi^*$	Tetrahedral planar
	419	23866	C.T	

Antimicrobial Activity:

The results of Schiff base ligand L₁ and its complexes against bacterial factors such as *Staphylococcus aureus*, a Gram-positive bacterium, and *Escherichia coli*, a Gram-negative bacterium, as well as fungi like *Candida albicans*, showed good biological efficacy. This indicates that the activity of the prepared complexes against various microorganisms is enhanced through the process of heavy metal removal with different biologically active metals, as illustrated in Table 4.

Table 4: The Biological Efficacy of Schiff Base and Its Complexes in mg.

compounds	<i>E.coli</i>			<i>Staphylococcus aureus</i>			<i>Canidia albicans</i>		
	25	50	75	25	50	75	25	50	75
L ₁	10	15	22	10	20	22	10	---	---

[Pt(L ₁) ₂ Cl ₂]	18	13	20	---	20	20	---	---	---
[Hg(L ₁) ₂]	---	---	8	---	12	25	---	---	---
[Zn(L ₁) ₂]	10	10	12	17	28	25	---	---	---

Adsorption of Complexes Using Bentonite: Effect of Contact time

The effect of time is considered one of the most important factors in the adsorption process. To determine the equilibrium time for the adsorption of platinum complex solution onto bentonite surface, the equilibrium time was studied at a temperature of 25°C and C=50 ppm, surface weight of 0.3 g, and grain size of 75 µm. The equilibrium time was found to be 60 minutes.

Table 5: Equilibrium Time for Bentonite Surface

C(ppm)	Time(min)	C _t (ppm)	q _e (mg/g)	Equilibrium time(min)
50	10	15.29	3.471	50
	20	11.92	3.808	
	30	10.69	3.931	
	40	10.67	3.933	
	50	11.68	3.832	
	60	11.68	3.832	
	70	11.68	3.832	

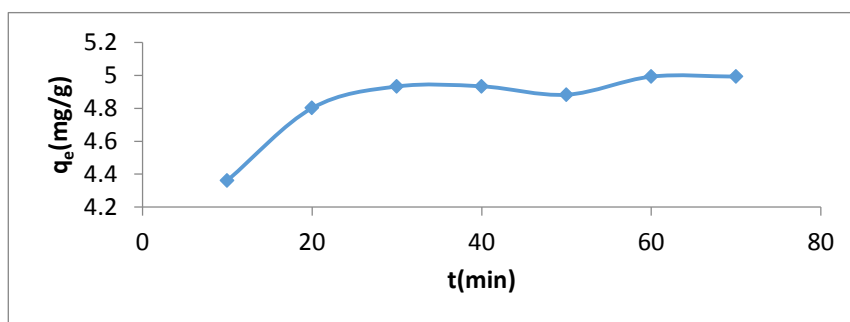


Figure 5: Effect of Equilibrium Time on Adsorption Capacity of Bentonite at 25°C

The Adsorption Isotherms

The adsorption of the complexes on the exterior of bentonite was examined within a concentration range of (5-50) ppm and at temperatures of (25, 35 and 45°C). The other influencing factors on the adsorption surface were fixed, such as the ideal weight (0.3g), equilibrium time (60 min), and grain size ≤75 µm. The adsorption capacity values were plotted against concentration at equilibrium to obtain the adsorption isotherms.

The study of adsorption isotherms is of great importance in describing the adsorption process as it provides information on the adsorption capacity of the adsorbent material with to its concentration. Through observing the above figure, it becomes apparent that the general shape of the adsorption isotherm is of type (S) according to the classification by Giles ⁽²⁰⁾. Additionally, through the (S) classification, the orientation of the adsorbed molecules on the surface can be determined to be perpendicular, occupying a smaller surface area, and thus resulting in higher adsorption ⁽²¹⁾. Furthermore, from observing the figure above, an increase in adsorption capacity with an increase in temperature can be seen, indicating that the adsorption process is heat-absorbing (endothermic).

Two typical models of adsorption isotherms were studied:

1. **Langmuir Isotherm Model:** The Langmuir isotherm model equation was applied and fitted to the data of the complex adsorption on bentonite at different temperatures. The adsorption isotherm data were graphically represented as follows:

The Langmuir

2. **The Freundlich isotherm model:** was applied to the data of the complex adsorption on bentonite at different temperatures. The Freundlich isotherm data were plotted graphically as shown in the following Table 6:

Table 6: presents the Langmuir and Freundlich isotherm constants and the correlation coefficient (R²) values for the complex to adsorb on bentonite in varying temperatures

	25°C			35°C			45°C		
Isotherm	Kl(L/mg)	q _e max (mg/g)	R ²	Kl(L/mg)	q _e max (mg/g)	R ²	Kl(L/mg)	q _e max (mg/g)	R ²
Langumuir	-0.9213	-4.2716	0.6717	-1.6098	- 3.7523	0.6062	-1.0868	-3.4965	0.6608
Freundlich	Kf(mg/g)	n	R ²	Kf(mg/g)	n	R ²	Kf(mg/g)	n	R ²
	0.1613	0.2804	0.8985	0.1987	0.2598	0.861	0.2325	0.2473	0.8709

From the results in the table above, the correlation coefficient (R²) values for the Langmuir model are lower than those for the Freundlich model at all temperatures can be observed. This confirms that the Freundlich model is more applicable than the Langmuir model ⁽¹⁸⁾. Additionally, the values of *Kf* increase with increasing temperature can be noticed, indicating that the adsorption layer is heat-absorbing ⁽²²⁾.

The effect of temperature on the adsorption process of the complex on the bentonite surface was studied and calculated at different temperatures (25, 35, 45°C), and the results were included in Table 8. Studying the effect of temperature in the adsorption process is of great importance as it enables us to calculate thermodynamic functions such as Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS), which help in better understanding the adsorption process. Gibbs free energy change is used to determine the spontaneity of the system, and enthalpy changes are used to determine the nature of the process, whether it is endothermic or exothermic. The change in entropy (randomness) indicates whether it increases or decreases during the adsorption process. The free energy change (ΔG) was calculated using the following equation⁽²²⁾:

$$\Delta G = -Rt \ln K_{eq} \text{ -----(3)}$$

Where

G= represents the change in Gibbs free energy of adsorption (KJ/mol).

R= the universal gas constant (8.314 J.mol⁻¹.K⁻¹).

K_{eq} = the equilibrium constant for the adsorption process, which is calculated at each temperature using the following equation:

$$K_{eq} = \frac{q_e \times W(g)}{C_e \times V(L)} \text{ ----- (4)}$$

Where: C_e: Concentration at equilibrium (mg/L); q_e: Amount of adsorption (mg/g); W: Weight of the adsorbent (g); V: Volume of the complex solution (L)

To calculate the enthalpy content (ΔH), it is done by plotting the values of the logarithm of the equilibrium constant $\ln K_{eq}$ versus the reciprocal of the temperature (1/T) according to the following equation:⁽²³⁾

$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \text{ -----(5)}$$

Where a linear relationship can be obtained, with the slope $\frac{-\Delta H}{RT}$ and the intercept equal to $\frac{\Delta S}{R}$.⁽²³⁾

Table 7: Thermodynamic equilibrium constants and functions values for the Pt complex's adsorption at various temperatures on the bentonite surface

T(K)	1/T(K ⁻¹)	lnK _{eq}	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS(J/mol.K)
298	0.00335	6.1388	-15.2093	80.5959	318.3430
308	0.00324	6.2019	-15.8812		
318	0.00314	8.2069	-21.6978		

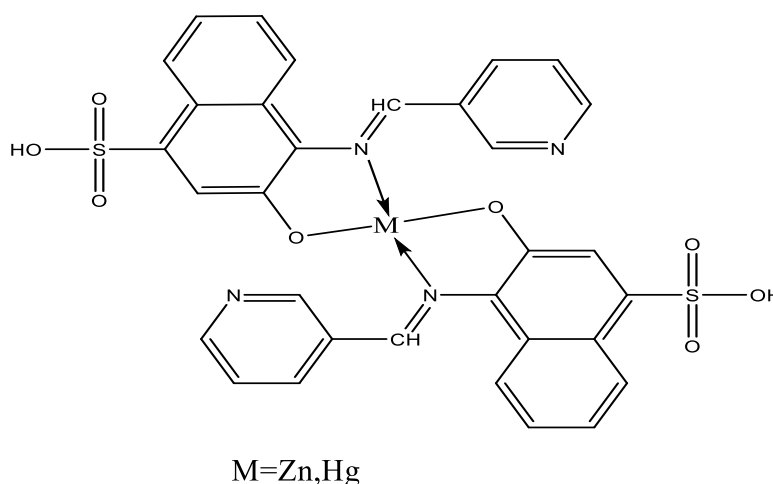
From the table above the following things can be concluded:

The values of the change in Gibbs free energy (ΔG) for the adsorption process are negative, indicating that the adsorption process is spontaneous⁽²⁴⁾. The value of ΔH is positive, suggesting that the adsorption process on the surface is endothermic. Also, the ΔH value is less than (40 KJ/mol), indicating that the adsorption is of a physical nature⁽²⁵⁾. The ΔS value is positive,

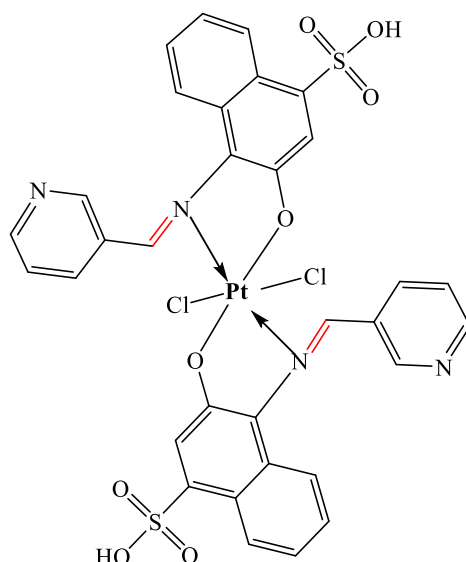
indicating that the interacting molecules of the adsorbed complex on the surface are more random compared to their state in the solution, suggesting a decrease in orderliness upon adsorption and absorption together ^(26,27).

Conclusions:

Three new Schiff base (Pt, Hg and Zn) complexes derived from primary aldehyde with 1-amino-2-naphthol-4-sulfonic acid was prepared and diagnosed by various methods. The results indicated that the ligand is coordinated with the metal ions via nitrogen imine group and oxygen (phenolic group), the proposed form of Hg and Zn is tetrahedral geometry and the form of Pt is octahedral geometry as show in scheme 2 and 3. The compounds were studied as antimicrobial and the values of thermodynamic functions (ΔH° , ΔS° and ΔG°) obtained indicated that the endothermic process for both system and a spontaneous and randomness increasing for Pt complex.



Scheme 2: The geometry of complexes



Scheme 3: The geometry of complexes

References

- [1] Magar, BHAUSAHEB K., A. S. Kirdanta, and K. K. Chondhekar (2013). "Formation of N-salicylidene-p-chloroaniline: A kinetic study." *Acta Chim. Pharm. Indica* 4.1: 40-46.
- [2] Mahdi, S. H., & Kareem, L. K. A. (2024). Synthesis, characterization, anticancer and antimicrobial studies of metal nanoparticles derived from Schiff base complexes. *Inorganic Chemistry Communications*, 112524.
- [3] Yousif, M., & Abdul Kareem, L. K. (2021). SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDY OF NEW COMPLEXES SCHIFF BASE DERIVED FROM 4-BROMO-2-METHYLANINE. *Biochemical & Cellular Archives*, 21.
- [4] Al-Hasnawi, F., Kareem, L. K. A., & Mortatha, D. M. (2023). Synthesis, Physicochemical Elucidation And Biological Screening Study Of New Ligand Derived From 5, 6-O-Iso Propylidene-L-Ascorbic Acid And Its Metal (II) Complexes. *Malaysian Journal of Science*, 45-55.
- [5] Rashid, K. W., Kareem, L. K., & Rasheed, M. K. (2022). Synthesis, Characterization and Bioactivity Study of Few Metal Complexes of Curcumin with 2-(1H-Benzimidazol-2-yl) Aniline. *Technology*, 12(3), 1076-1080.
- [6] Qin, Wenling. (2013) "Schiff bases: A short survey on an evergreen chemistry tool." *Molecules* 18.10: 12264- 12289.
- [7] HadeerJasem, A. G. H. (2021). Enhanced the antioxidant activity of 1-amino-2-naphthol-4-sulfonic acid by complexation with organotin (IV) compounds. *Annals of the Romanian Society for Cell Biology*, 25(6), 6182-6193.
- [8] W. A. (2023) "Anti-Cancer and Thermal Study of New Derivatives of Sulfonic Acid as a Schiff Base with [Pt (II) and Pd (II)] Complexes" Available at SSRN 4482216.
- [9] Bakare, Safyah B. (2019) "Cu (II), Co (II), Ni (II), Mn (II) and Zn (II) Schiff base complexes of 3-hydroxy-4-[N-(2-hydroxynaphthylidene)-amino]-naphthalene-1-sulfonic acid: Synthesis, Spectroscopic, thermal, and antimicrobial studies." *Polish Journal of Chemical Technology* 21.3: 26-34.

- [10] Pathan, H. K., Fatima, A., Garg, P., Muthu, S., Yadav, A., Siddiqui, N., & Javed, S. (2023). Spectroscopic, Computational, Molecular Docking and Dynamics Simulations Studies of 4-Amino-3-hydroxyNaphthalene-1-Sulfonic Acid (ANSA). *Polycyclic Aromatic Compounds*, 1-20.
- [11] Mohammed, S. S., Karem, L. K. A., Salman, S. A., & Al-Darwesh, M. Y. (2020). SPECTROSCOPIC, THERMODYNAMIC AND KINETIC STUDIES OF LIGAND COMPLEXES DERIVED FROM 2-AMINOTHIOPHENOL. *Biochemical & Cellular Archives*, 20(2).
- [12] Mahdi, H. T., & Rasheed, M. K. (2023). Synthesis and Identification of Thiazines-4-on Derived from Sulfamethoxazole, and Testing of some of their Antibacterial Properties. *Journal of New Materials for Electrochemical Systems*, 26(3).
- [13] Al-Obaidy, G. S., Ibraheem, K. R., & Mesher, M. F. (2020). Metal complexes derived from dithiocarbamate ligand: formation, spectral characterization and biological activity. *Systematic Reviews in Pharmacy*, 11(6), 360-368.
- [14] Ran, Xueguang, et al. (2010): "Syntheses, characterization and biological studies of zinc (II), copper (II) and cobalt (II) complexes with Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and selenomethionine." *Applied Organometallic Chemistry* 24.10741-747'.]
- [15] Silverstein R. M. and Webster F. X., "Spectroscopic Identification of Organic Compounds".(1996) 6th Ed, John Wiley and Sons, Inc., New York : 401-406.
- [16] Amer A. A. and Karem, L. K. (2023) "Synthesis, Characterization, Antimicrobial and Antioxidant Study of New Complexes Schiff Base Derived from 2, 5-diChloroaniline." *International Journal of Drug Delivery Technology*: 13(2) 686-691.
- [17] Lever A. B. P., *Inorganic Electronic Spectroscopy*. New York; (1968): 121.
- [18] Wang, Q., Liao, M., Lin, Q., Xiong, M., Mu, Z., & Wu, F. (2021). A review on fluorescence intensity ratio thermometer based on rare-earth and transition metal ions doped inorganic luminescent materials. *Journal of Alloys and Compounds*, 850, 156744.
- [19] Hu, Q., Lan, R., He, L., Liu, H., & Pei, X. (2023). A critical review of adsorption isotherm models for aqueous contaminants: Curve characteristics, site energy distribution and common controversies. *Journal of Environmental Management*, 329, 117104.
- [20] Carrales-Alvarado, D. H., Rodríguez-Ramos, I., Leyva-Ramos, R., Mendoza-Mendoza, E., & Villela-Martínez, D. E. (2020). Effect of surface area and physical-chemical properties of graphite and graphene-based materials on their adsorption capacity towards metronidazole and trimethoprim antibiotics in aqueous solution. *Chemical Engineering Journal*, 402, 126155.
- [21] Kipling J. J. (1965). Adsorption From Solutions of Non – electrolytes. Academic press London ,P.P:129-133,P.P:10-184.
- [22] Basma.(2011).clay-polymer Nano composites as Adsorbent for same organic pollutants, MSc. Thesis-university of Baghdad.
- [23] Peng,x. ,Huang,D.,Odoom-Wubah,T.,Fu,D.,Huang,J.,& Qin,Q.(2014).Adsorption of anionic and Cationic dyes on Ferromagnetic ordered meso porous carbon from aqueous solution: equilibrium, thermodynamic and Kinetics. *Journal of Colloid and Inter face Science*, 430,272-282.

- [24] Umpierres, C. S., Prola, L. D., Adebayo, M. A., Lima, E.C., DosReis, G.S., Kunzeler D.D., & Benvenuti, E.V. (2017). Mecoporous Nb₂O₅/SiO₂ material obtained by-sol-gel method and applied as adsorbent of crystal violet dye. *Emvironmental technology*, 38(5), 566-578.
- [25] Melichova, Z. Hromada, L. Luptakova. A. (2014), "removal of pb⁺² ions From aqueous solytions
- [26] Al Nasir, H. A., & Mohammed, S. S. (2023). Experimental Investigation on Adsorption of Methyl orange Using eggshells as adsorbent Surface. *Ibn AL-Haitham Journal For Pure and Applied Sciences*, 36(1), 197-207.
- [27] Mohammed, S. S., & Aljebur, L. A. (2023). Corrosion Inhibition of Medium Carbon Steel in the Acidic Medium Using Alcoholic and Aqueous Extract of Kujarat Tea Plant. *Baghdad Science Journal*, 20(4), 1297-1297.