



Thermodynamic Studies of $[M^{+2}]$ Complexes with 3-Hydroxy-2-(3-(4-Nitrobenzoyl) Thiouriedo) Propanoic Acid

Taghreed Baqer Alwan^{1*}, Basima M.Sarhan², Wedyan Mansoor Obaid³
, Abbas M. Abbas⁴, and Mohamed Abdel-Raheem Ali Abdel-Raheem⁵

^{1,3}Department of Chemistry, College of Education for Pure Sciences (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq.

²General Education in Baghdad Rusafa First, Distinguished High School, Baghdad, Iraq.

⁴Ministry of Education General Directorate for Education in the Province of Maysan, Maysan, Iraq.

⁵Pests & Plant Protection Department, Agricultural and Biological Research Institute, National Research Centre, Egypt.

* Corresponding Author.

Received: 5 January 2024

Accepted: 23 August 2023

Published: 20 January 2025

doi.org/10.30526/37.1.3175

Abstract

In the current research work, the prepared new ligand 3hydroxy-2-(3-(4-nitro-benzoyl) thiouriedo) propanoic acid (NTP) has undergone synthesis through the reactions of 4-nitrobenzol isothiocyanate with the serine amino acid; its complex has been studied by effects of the temperature ranging within (25-45 °C) and various concentrations on molar conductivity values from Arinus' law application, by which decomposition constant and uniform molar conductivity is determined. The thermodynamic parameters (i.e., ΔS , ΔG , and ΔH) have been estimated and then discussed. Results have shown that the level of the molar conductivity increases with the degree of temperature and decreases with the increase of the concentration using solvent (DMSO). The dissociation process is exothermic; that ligand's transition metal complex has been synthesized and then characterized through the UV-Vis spectra, FTIR, conductivity measures, and magnetic susceptibility. The general formula $[M(NTP)_2]$, $M^{+2} = (Cu)$, is that the molecular form for those complexes is tetrahedral, except that the copper is of a square planer.

Keywords: Isothiocyanate, 4-nitrobenzoyl, serine, thermodynamic measurements, transition metals.

1. Introduction

Amino acids are the building blocks of proteins. They're Indispensable due to their biological functions, as defined by the roles of enzymes (1,2). Amino acids, in particular, significantly impact cell structure, tissue repair, and antibody synthesis,



resisting various bacteria and virus types. They also interfere in manufacturing numerous compounds, such as enzymes, pigments, and hormones. In addition, they represent an intermediate cellular metabolism state (3, 4).

Transition metal complexation as an electron acceptor with various electron donor bases, including acceptor to form charge-transfer complex, has been studied in detail; serine can be defined as an unbalanced or neutral polar amino acid class (5,6). This research has shown that with the increase of the concentration, the degree of the molar conductivity is decreased. In contrast, the degree of conductivity will increase with the rise in temperature. By applying the Arrhenius equation (7,8).

The results of this study include ligand stability, its complexes, and the fact that they're heat-emitting (9,10).

The aim of the present study is to determine the value of the molar conductivity at temperature degrees in the range of (25-45) °C and various concentration levels, utilizing DMSO solvent and noting variations and results of this work.

2. Materials and Methods

2.1. Ligands and complexes

The ligand, as well as its Ni complex, have been prepared by (11), on which all of the measurements that the researcher needs have been made:

- The ^1H and ^{13}C NMR have been recorded by utilization of the Ultrashield 300MHz Switzerland at Univ. of Al al-Bayt, Jordan.
- The melting point had been recorded by utilization of melting point meter KRUSS (A, KRUSS OPTRONIC).
- The FTIR spectra have been noted as FTIR with the use of the 3800 Shimadzu in ranging within ($4,000\text{ cm}^{-1} - 400\text{ cm}^{-1}$) with the use of the (KBr) disc.
- The electronic spectra had been obtained with utilizing (UV160 Shimadzu) spectrophotometer at a temperature of 25 °C for 10^{-3} M DMSO of Solution.
- The Molar Conductivity had been measured at 25 °C temperature for 10^{-3} M with the use of Philips PW.

that has been operated upon through making the physical measures that were denoted by thermodynamic functions (ΔH , ΔG , and ΔS).

2.2. Physical measurements

The DMSO solvents have measured conductivity values using the PHILIPS PW-9526 digital conductivity meter with 0.829 cm^{-1} cell constant. A variety of the concentrations (10^{-3} - 10^{-4}) molar has been measured at a temperature of (25-45) °C; in addition to that, the concentration levels in the range of (0.10-0.50) g/L have been worked out.

Molar conductivities of ligands and solutions have been evaluated at various concentrations and temperature degrees within (25-45) °C, and the specific molar conductivity has been obtained by subtracting the conductivity of the solvent from the conductivity of solutions.

The results found that higher concentrations lead to lower conductivity levels, and the other way around concerning temperatures, higher molar conductivity increased,

which is why it has been concluded that it's the ligand and complex that exothermic process.

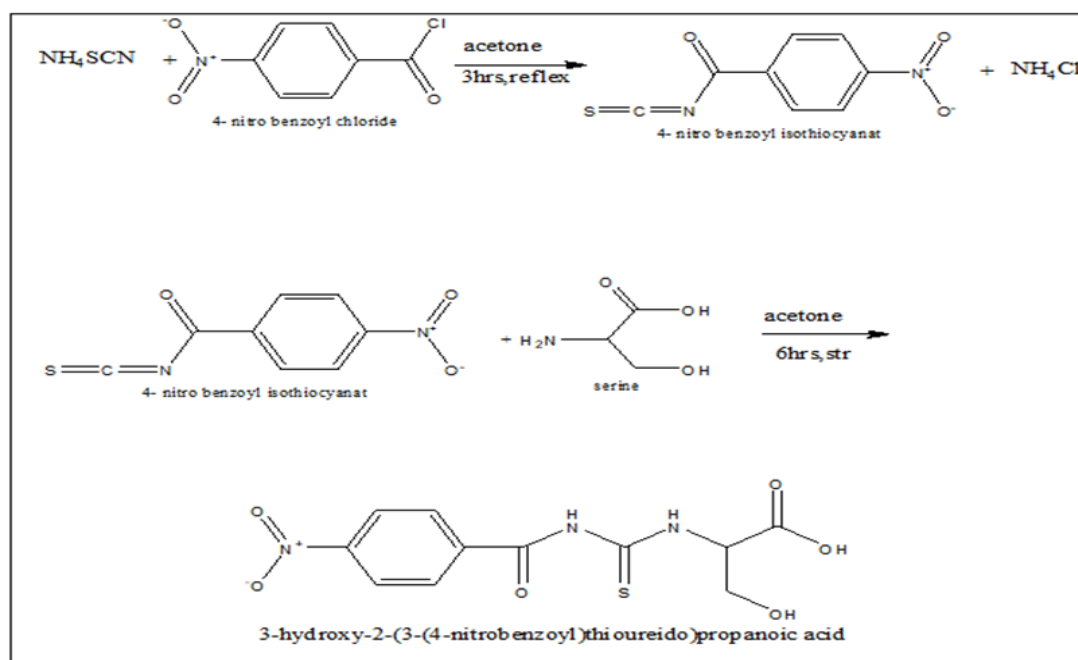
2.3. Ligand (NTP) preparation

2.3.1. Preparing 4-nitro benzoyl isothiocyanate (12)

The process begins by dissolving (4.82 g, 26 Mmole) of the 4-nitro benzoyl Chloride in 15 mL of the acetone and (2 g, 26 Mmole) of the ammonium thiocyanate in 25 mL acetone, which has been mixed by the stirring for 3hrs, followed by filtering, filtrate has been utilized for a following reaction.

2.3.2. Preparing of 3-hydroxy-2-(3-(4-nitro-benzoyl) thiouriedo) propanoic acid (13)

The preparation began by dissolving (2.77 g, 26 Mmole) of amino acid (i.e. serine) in 15ml of the acetone and former solution has been added into it, and after that, this mix had been refluxed and stirred for 6hr. The resultant solid has been obtained, followed by washing by using acetone and recrystallized from the ethanol (mp=148-150) °C, yield=80%, as shown in **Scheme 1**. %C resulted (42.470) whereas calculated 42.170, %H had resulted (3.144) whereas calculated (3.510), %N resulted (13.770) whereas compute (13.410) and %S found (10.115) whereas calculated (10.220). which has been agreement with proposed formula ($C_{11}H_{11}N_3O_6S$).



Scheme 1. The route of the synthesis for preparation ligand (NTP).

3. Results and Discussion

The ligand and its complex are solid and have stability relative to the air's moisture. They are decomposed at a high degree of temperature (232-233) °C, and they have a lower level of solubility in the methanol, the ethanol as solvents, however, soluble in the DMSO, which has been listed in **Table 1**. The NTP's molar conductivity with some of their metal complex in the DMSO solvent has been listed

in **Table 1**. Molar conductivity values indicate non-electrolyte behaviors of those complexes (13). All metal chelates have a stoichiometry of 1:2 (metal: ligand) from analysis of atomic absorptions.

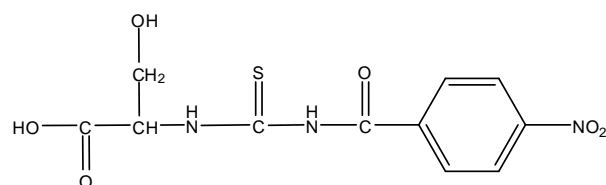
Table 1. Features and analyses of ligand and their complex.

Compounds	M.wt (gm/mole)	Colour	M.P(C) Ordeco.	M% Calculations (Found)	Molar Cond.Ohmm ⁻¹ cm ² mol ⁻¹ In DMSO	μ_{eff} (BM)
C ₁₁ H ₁₁ N ₃ O ₆ S NTP	313	Dark-yellow	148-150	-----	0.420	-----
[Cu(NTP) ₂]	687.5	Green-yellow	162	9.23 (9.21)	4.56	1.71

3.1. Spectral data

3.1.1. The ¹H-NMR spectra of NTP

The ¹H NMR spectra of the NTP ligand have been illustrated in **Figure 1**, which shows the signals below:



Malty signals because of the DMSO solvent in the range of δ (2.098ppm-2.509 ppm), the spectrum had shown triplet signal at a value of δ (1.549ppm) for (1H,CH), and doublet signal at the value of (δ 3.430ppm) to (2H,CH₂), singlet signal at a value of (δ 4.912ppm) for (1H,OH), so singlet at (δ 7.680ppm) because of the (1H, NH_{thiourea}), singlet at the value of δ (8.082ppm) because of the (1H, NH_{amid}), a doublet signal at the range of δ (8.111ppm-8.364ppm) for (4H,_{aromatic}), and singlet signal at (11.287ppm) for (1H, COOH). **Table 2** lists signals of the chemical shifting by the ppm for the NTP (14).

Table 2. The ¹HNMR and chemical shifting by the ppm for an NTP.

Compounds	Functional groups	(ppm) δ
ANP	t(1 H,CH)	1.549
	d(2H,CH ₂)	3.480
	S(1 H,OH)	4.912
	S (1 H, NH amine)	7.680
	S(1 H, NH sec amide)	8.082
	(d-d)(4 H, _{aromatic} proton)	(8.111-8.364)
	S (1 H,COOH)	11.287

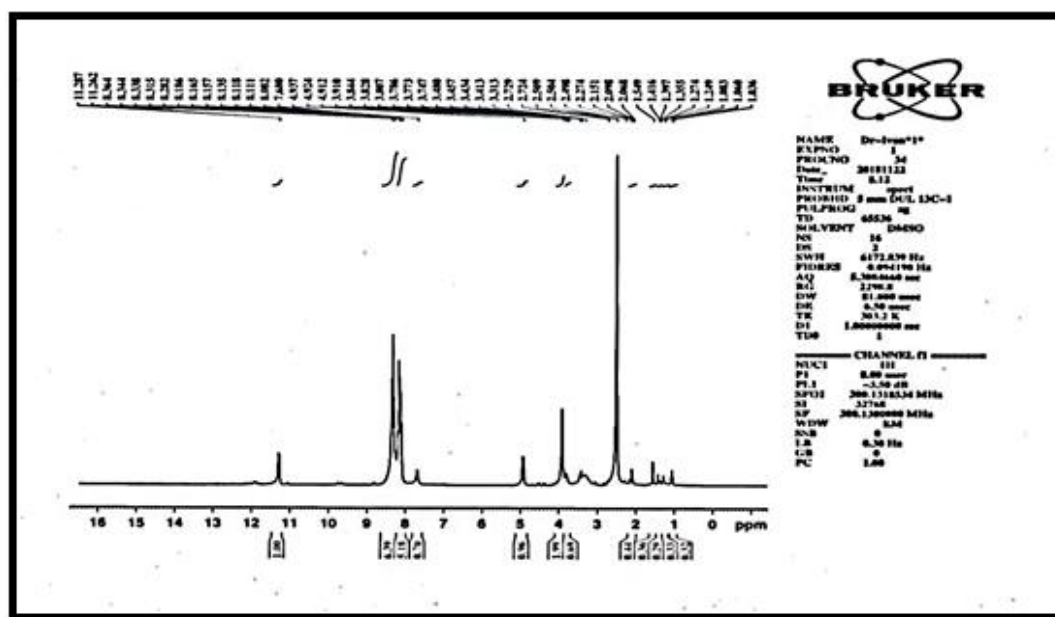


Figure 1. The ¹H NMR spectrum of the ligand (NTP).

3.1.2. The ¹³C NMR spectra for NTP

The ¹³C NMR spectrum for NTP ligand in **Figure 2** had shown the signals below: signals in the range of δ (38.69ppm-40.3560ppm) for the solvent di-methylsulfoxid (DMSO), and singlet signal at the value of (δ 59.49ppm) for (CH₂), and other signals at the value of (δ 60.4ppm) to (CH), and multi-signals in the range of δ (123.296 ppm-149.804ppm) for the (4C_{aromatic}), singlet peak at the value of (δ 166.168 ppm) because of (C=O_{sec amide}), and singlet peak at the value of (δ 170.582ppm) for (COOH), and singlet peak at the value of (δ 179.981) for (C=S). **Table 3** shows signals of the chemical shifting by the ppm for the NTP (15).

Table 3. The ¹³C NMR in DMSO solvent chemical shifting by the ppm.

Compounds	Functional groups	δ (ppm)
ANP	S (C,CH ₂)	59.490
	S (C,CH)	60.400
	M (C, aromatic)	(123.296-149.804)
	S (C=O sec amine)	166.168
	S (COOH)	170.582
	S (C=S)	179.981

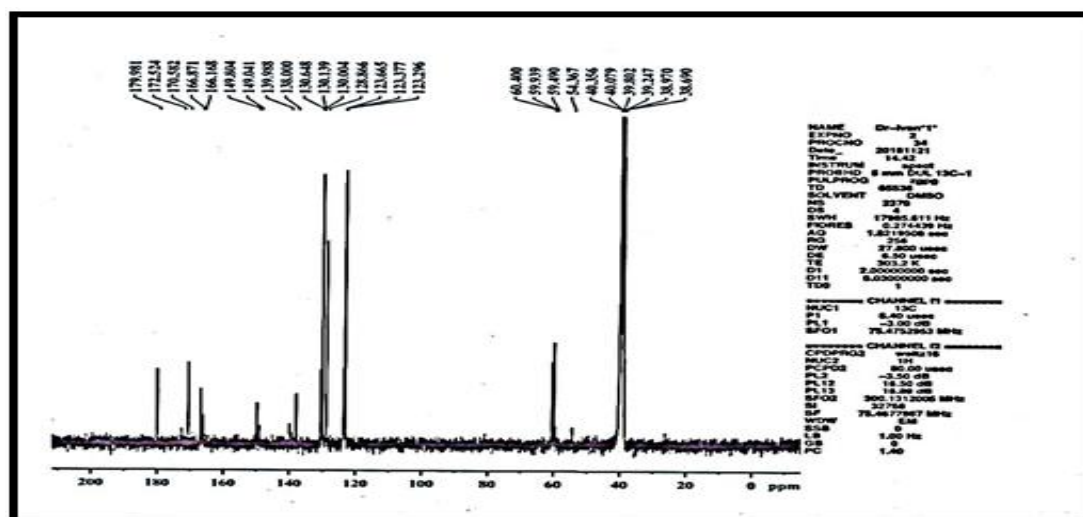


Figure 2. The ^{13}C -NMR spectrum of NTP ligand.

3.1.3. Magnetic characteristics of metal complexes

Magnetic moment (μ_{eff}) for the $\text{Co}^{+2}(\text{d}7)$ and $\text{Mn}^{+2}(\text{d}5)$ complex have been equal to (4.530)BM and (5.880)BM, respectively, which is in the range of expected spin-only values. The greater μ_{eff} value of $\text{Ni}^{+2}(\text{d}8)$ complex (3.110)BM because of orbital contributions. Magnetic moment value μ_{eff} of $\text{Cu}^{+2}(\text{d}9)$ complex has been estimated to be equal to (1.710) BM which is within expected values to 1 electron (16-18), as shown in **Table 4**.

Table 4. Some of physical characteristics of ligand (NTP) as well as their metal complex.

Compounds	M.wt (gm/mole)	Colour	MP(C) or dec.	M% Calculation (Found)	Molar Cond. Ohm^{-1} $\text{cm}^2\text{mol}^{-1}$ in DMSO	μ_{eff} (BM)
$\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_6\text{S}$ (NTP)	313	Dark- yellow	148-150	-	0.420	-
$[\text{Cu}(\text{NTP})_2]$	687.5	Green- yellow	162	9.23 (9.21)	4.56	1.71

3.1.4. Electronic spectrum

The spectrum of NTP ligand, which has been depicted by **Figure 3** shows the bands at $(36,363\text{cm}^{-1}$ and $26,455\text{cm}^{-1}$ because of $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ respectively (18).

$[\text{Cu}(\text{NTP})_2]$ complex:

Spectra of a green-yellow Cu(II) complex had shown 2 bands at 36900 cm^{-1} and 12106 cm^{-1} attributed to ligand-field as well as ${}^2\text{B}_{1g} \longrightarrow {}^2\text{A}_{1g}$ [18].

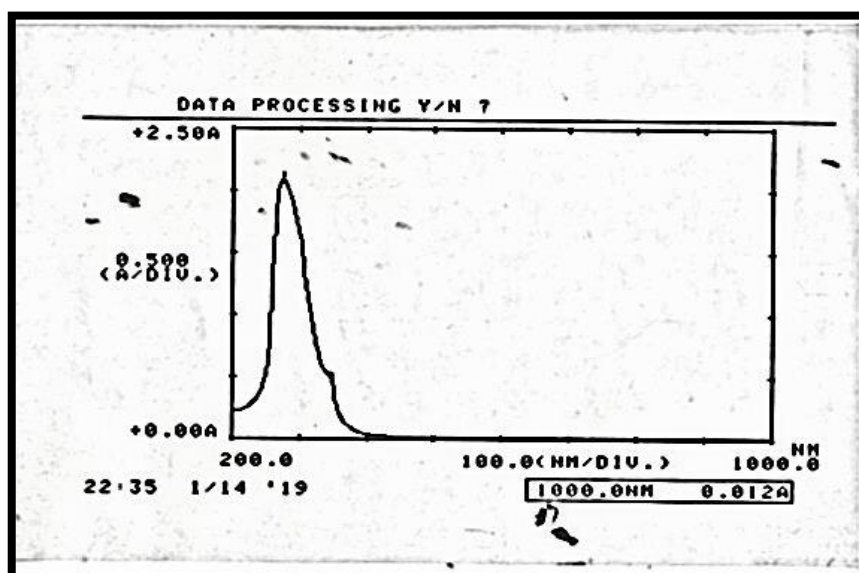


Figure 3. The UV -vis spectrum for ligand (NTP).

3.1.5. The FTIR spectra

Characteristic vibrations of the ligand (NTP) as well as their complex as the KBr disc have been listed in **Table 5**. Free ligand (NTP) spectrum, which has been depicted by fig1, had shown the medium band at the value of 3417 cm^{-1} and that may be a result of $\nu(\text{N-H})$, whereas other medium band at the value of 3178 cm^{-1} because of (OH) . Other band at 1728 cm^{-1} that belongs to $\nu(\text{COO})_{\text{asym}}$ and 1346 cm^{-1} for $\nu(\text{COO})_{\text{sym}}$, strong band at the value of $\nu 1670\text{ cm}^{-1}$ because of $\nu(\text{C=O})$ group, $\nu(\text{C=S})$ have been found at the value of $1,257\text{ cm}^{-1}$ (9,10). FTIR spectrum of the complex that have been prepared had shown $\nu(\text{N-H})$ in between $(3,460\text{ and }3,417)\text{ cm}^{-1}$ that exhibits shifting to higher frequency values when compared to proposed free ligand. The likelihood of ligand coordination by a nitrogen atom at amine group (19,20). The absorption that was assigned for the $\nu(\text{COO})_{\text{sym}}$ has been observed at range of $(1400\text{-}1419)\text{ cm}^{-1}$ shifted to greater values of the frequency by $(54\text{-}73)\text{ cm}^{-1}$. Whereas band that has been a result of $\nu(\text{COO})_{\text{asym}}$ had been noticed in the range of $(1624\text{-}1604)\text{ cm}^{-1}$ had shifted to lower frequency values by $(104\text{-}124)\text{ cm}^{-1}$ and that had indicated attached carboxylic group to central metal ion (13,14). Bands of stretching vibration $\nu(\text{C=S})$ as well as the $\nu(\text{C=O})$ carbonyl group have shown very little to no changes in the frequency values, thus, which is an indication of the fact that they don't coordinate to metal ion (21). The bands of metal-oxygen and the metal-nitrogen have been confirmed by existence of $\nu(\text{M-N})$ as well as the $\nu(\text{M-O})$ stretching vibrations in a range of $(520\text{-}423)\text{ cm}^{-1}$ and $(486\text{-}432)\text{ cm}^{-1}$ respectively, as shown in **Figure 4**.

Table 5. Values of the FTIR absorption by cm^{-1} units of (NTP) with the complex

Compounds	(COO)U asym	(COO)U Sym	$\Delta\nu(\text{NH})$ U (OH)U	(C=O)U	(MO)U	(C=S)U	(MN)U
NTP	1728(S)	1.346(S)	---	3417(M) 3178(M)	1670(S)	---	1257(M)
[Cu(NTP) ₂]	1604(M)	1.418(M)	186	3458(b)	1676(M)	482(M)	1261(M)

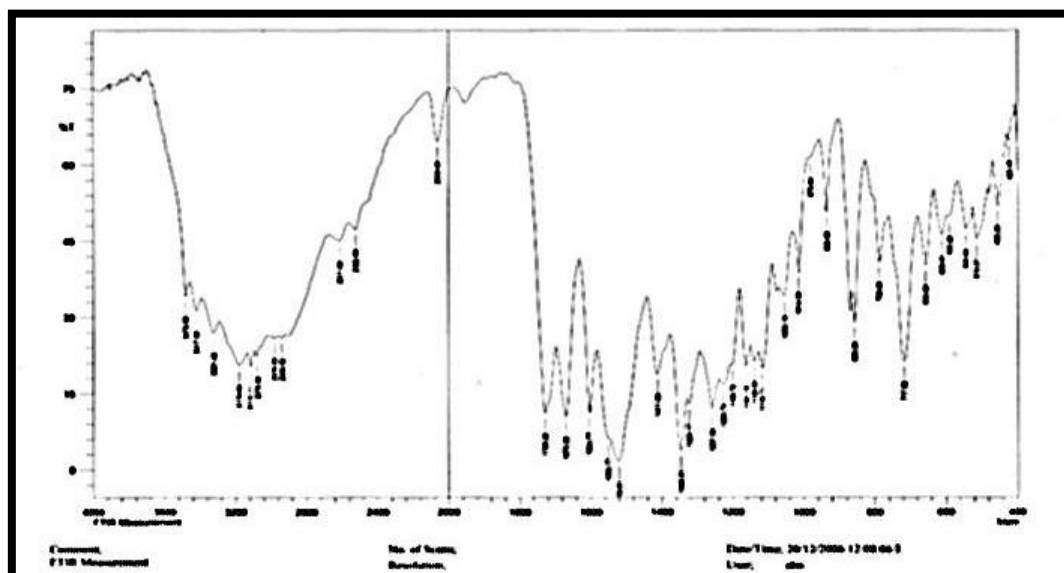


Figure 4. Infrared spectrum of ligand (NTP)

3.2. Thermodynamics study

3.2.1. Effects of various concentration levels on the degree of the molar conductivity

Values of molar conductivity of the ligand (NTP) as well as its complex $[Cu(L)_2]$ have been obtained in a DMSO solvent at various concentration levels and temperature degrees, which had been listed in **Tables 6** and **7**.

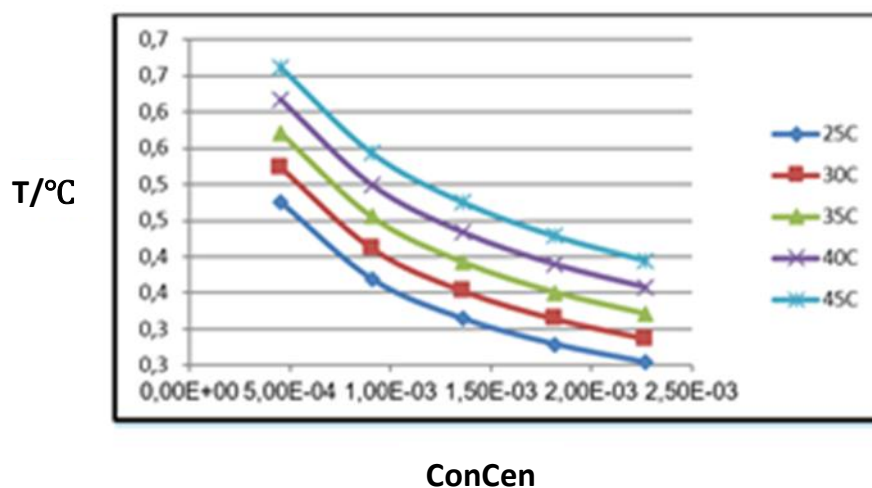
Table 6. The values of conductivity of (NTP) in DMSO at various concentration and temperatures.

NTP					
25 °C			30 °C		
C (g/L)	C(M)	S (mho)	C (g/L)	C(M)	S (mho)
0.10	3.55 E-04	6.72 E-07	0.10	4.55 E-04	1.07 E-07
0.20	8.09 E-04	0.36 E-06	0.20	8.08 E-04	0.53 E-07
0.30	1.36 E-03	0.74 E-06	0.30	1.36 E-03	2.85 E-07
0.40	1.84 E-03	2.09 E-06	0.40	1.87 E-03	2.97 E-07
0.50	6.28 E-03	6.34 E-06	0.50	5.25 E-03	3.82 E-07
35 °C			40 °C		
C (g/L)	C(M)	S (mho)	C (g/L)	C(M)	S (mho)
0.10	3.55 E-04	1.32 E-07	0.10	3.55 E-04	1.51 E-07
0.20	8.09 E-04	2.05 E-07	0.20	8.09 E-04	2.40 E-07
0.30	1.36 E-03	2.60 E-07	0.30	1.36 E-03	3.00 E-07
0.40	1.87 E-03	3.16 E-07	0.40	1.87 E-03	3.80 E-07
0.50	3.25 E-03	3.60 E-07	0.50	3.25 E-03	4.30 E-07
45 °C					
C (g/L)	C(M)	S (mho)			
0.10	3.55 E-04	1.60 E-07			
0.20	8.09 E-04	2.75 E-07			
0.30	1.36 E-03	3.20 E-07			
0.40	1.87 E-03	3.95 E-07			
0.50	3.25 E-03	5.20 E-07			

Table 7. The values of conductivity of the complex [Cu (L) ₂] in DMSO at various concentration and temperatures.

[Cu(L) ₂]					
25 °C			30 °C		
C (g/L)	C(M)	S	C (g/L)	C(M)	S
0.10	1.80 E-04	9.31 E-08	0.10	2.10 E-04	2.19 E-08
0.20	5.65 E-04	1.25 E-07	0.20	3.65 E-04	2.90 E-08
0.30	6.70 E-04	1.82 E-07	0.30	6.70 E-04	3.15 E-08
0.40	7.27 E-04	1.90 E-07	0.40	7.29 E-04	4.80 E-08
0.50	9.12 E-04	2.09 E-07	0.50	9.12 E-04	5.84 E-08
35 °C			40 °C		
C (g/L)	C(M)	S	C (g/L)	C(M)	S
0.10	2.80 E-04	4.59 E-08	0.10	1.80 E-04	7.40 E-08
0.20	3.45 E-04	6.80 E-08	0.20	3.95 E-04	1.32 E-07
0.30	5.90 E-04	8.35 E-08	0.30	4.30 E-04	1.81 E-07
0.40	8.29 E-04	1.70 E-07	0.40	7.27 E-04	2.79 E-07
0.50	9.12 E-04	1.84 E-07	0.50	8.90 E-04	3.10 E-07
45 °C					
C (g/L)	C(M)	S			
0.10	1.8 E-04	9.01 E-08			
0.20	3.65 E-04	1.8 E-07			
0.30	5.7 E-04	2.45 E-07			
0.40	8.27 E-04	3.73 E-07			
0.50	9.12 E-04	4.1 E-07			

Figures 5-8. show the decrease in molar conductivity value of ligand (NTP) as well as its complex [Cu(L)₂] the last concentration levels of natural solution consistent with behaviors of electrolyte solutions.



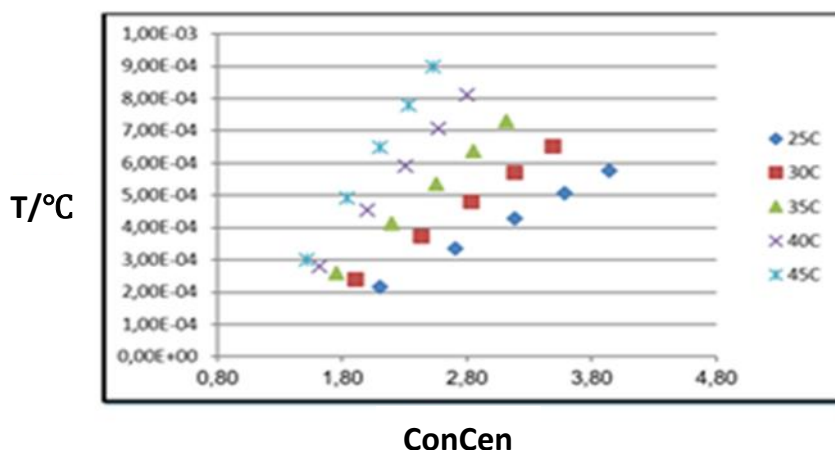


Figure 5. A decrease in values of molar conductivity of the (NTP) through the increase of concentration of solution and at various temperatures.

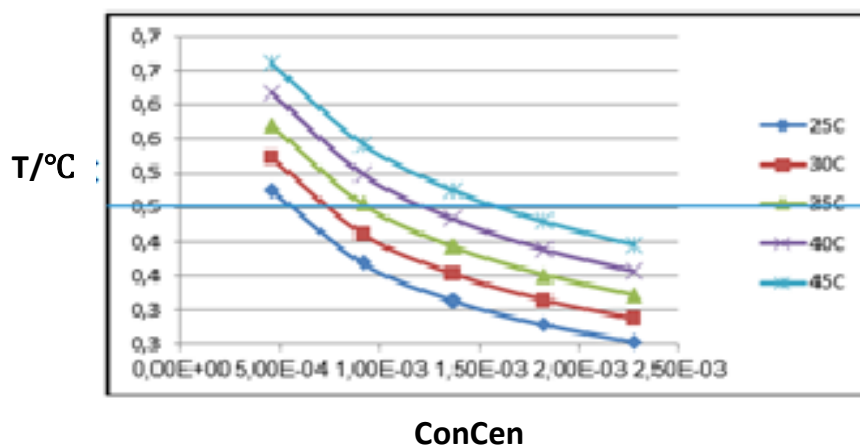


Figure 6. The correlation of concentrations to reciprocal of the conductivity of ligand (NTP) with the increase in the concentrations of the solution with various temperatures.

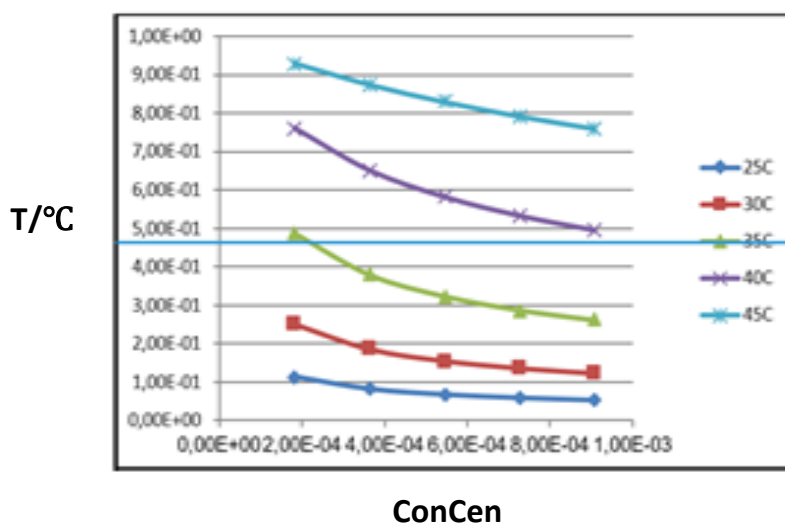


Figure 7. A reduction of values of molar conductivity of $[Cu(L)_2]$ complex with an increase in solution concentrations at various temperatures.

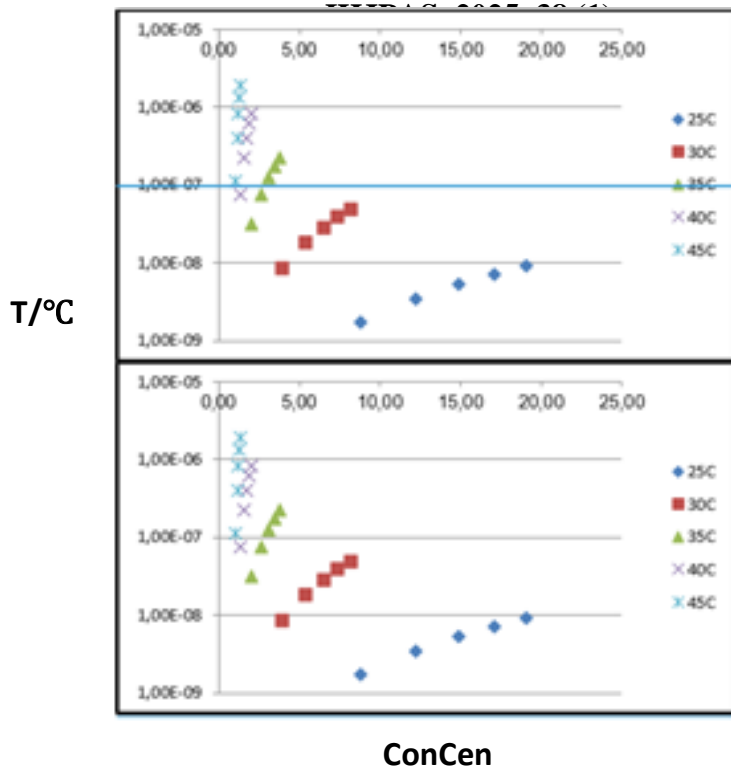


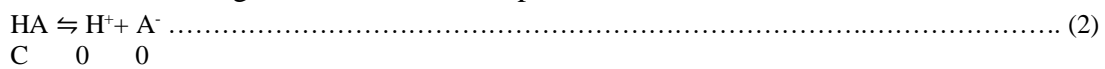
Figure 8. The correlation of concentrations with reciprocal of molar conductivity of [Cu(L)₂] complex through an increase of solution concentration with various temperatures.

3.2.2. Effect of temperature degree on the level of the molar conductivity

Concerning effects of the degree of temperature on the value of the conductivity (22), it has been observed that the two systems result in increasing molar conductivity value with the increase of the degree of the temperature, and based on what has been stipulated by Arinus relationship (23,24), Arinus correlation for the conductivity as in formula below:

$$\Lambda = e^{-E_a/RT} \dots\dots\dots (1)$$

Constant of hydrolysis equilibrium of the (NTP) as well as its complex [Cu(L)₂] have been obtained via basic correlation of the dissociation and the complex of both solutions of the ligand, which can be expressed below:



$$c(1-\alpha) \quad \alpha c \quad \alpha c$$

$$K_L = \frac{\alpha^2 C}{1-\alpha} \dots\dots\dots (3)$$

$$\alpha = \frac{\Lambda}{\Lambda_0} \dots\dots\dots (4)$$

$$K_L = \frac{(\frac{\Lambda}{\Lambda_0})^2 C}{1-\frac{\Lambda}{\Lambda_0}} \dots\dots\dots (5)$$

The linear form that has been adopted for the extraction of values of K_L and Λ_0 for the ligand has been:

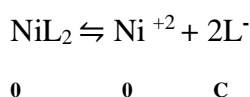
$$\Lambda C = \Lambda_0^2 K_L (1/\Lambda) - \Lambda_0 K_L \dots\dots\dots (6)$$

As this relationship's slope = $\Lambda_0^2 K_L$ and relationship has been intersected = $\Lambda_0 K_L$ Where values of those constants were listed in **Table 8**.

Table 8. The specific values of molar conductivity Λ_0 and arinus constant for every one of ligands (NTP) as well as its complex $[Cu(L)_2]$ at an absolute temperature.

T(K)	NTP		Cu(L) ₂	
	K	Λ_0	K	Λ_0
298	5.96457E-06	93.626	4.2E-08	60.572
303	3.89825E-06	80.510	2.43E-07	75.213
308	4.14254E-06	134.524	5.23E-06	88.743
313	4.26742E-06	184.105	5.25E-06	92.788
318	5.6239E-06	191.730	2.8E-05	190.423

Concerning correlation of the constant of complex decomposition $[Ni(L)_2]$ (25), it has been as below:



$$2\alpha c \quad \alpha c + \alpha c \quad 2\alpha c \quad \alpha c \quad C(1-\alpha)$$

$$K_{\text{cplx}} = \frac{4 \alpha^3 C^2}{C(1-\alpha)^3} = \frac{4 \alpha^3 C^2}{(1-\alpha)^3} \dots\dots\dots (7)$$

$$K_{\text{coplx}} = \frac{4\left(\frac{\Lambda}{\Lambda_0}\right)^3 C^2}{1 - \frac{\Lambda}{\Lambda_0}} \cdot \left(\frac{\Lambda_0}{\Lambda}\right)^3 \dots\dots\dots(8)$$

$$K_{\text{coplx}} = \frac{4 \Lambda^3 C^2}{\Lambda_0^3 - \Lambda \Lambda_0^2} \dots\dots\dots(9)$$

$$4(\Lambda C)^2 = \left(K_{\text{coplx}} \Lambda_0^3 \left(\frac{1}{\Lambda}\right) - K_{\text{coplx}} \Lambda_0^2\right) \dots\dots\dots(10)$$

Eq10 represents linear form of [Cu (L)₂] decomposition correlation, where through the plotting of 4 (Λ C)² on y-axis (Y) vs. ((1/Λ)) on x-transformer (X), the result is straight line which can be expressed as:

It has been noted in **Table 9**. that (Λ₀) values for the (NTP) are generally low and particularly through the comparison with (Λ₀) values for weak electrolytes in the aqueous solutions, as a result of the mechanism of a transport of dissolved proton in the DMSO, which isn't compatible with mechanism of proton transportation. In the aqueous solutions, specific value of molar connection (Λ₀) value of lycand solution (NTP) and at different temperature degrees is higher when compared to that of complex [Cu(L)₂].

Even though specific value of molar conductivity (Λ₀) of proton is low (because of difference in solvent), it is still high in comparison with other ions because of a small proton size as well as its small mass, i.e., low intrinsic inertia. Which is why, specific molar conductivity (Λ₀) of the solutions of the ligand (NTP) that has been considered as weak acid, it's larger when compared to that of the [Cu (L)₂] complexes.

Concerning values of constants of the (NTP) and its complex [Cu (L)₂], it has been noticed that in the case of the ligand (NTP), they're within normal weak acid dissolution constant value limits and difference of the solvent didn't alter that nature because of considered (DMSO) substance polarity. Although complex [Cu (L)₂] values are low, they have been considered high when compared to the corresponding decomposition constants in the aqueous solutions.

3.3. Thermodynamic function

Thermo-dynamic functions (26) of ligand (NTP) degradation and its complex [Cu(L)₂] have been obtained by the basic relationships below:

$$\Delta G = - RT \text{Ln}K \dots\dots\dots(11)$$

$$\text{Ln}K = (-\Delta H/R) \times (1/T) + (\Delta S/R) \dots\dots\dots(12)$$

On the other hand, through the plotting of **Eq. 12** (Ln K) vs. (1/T), the result is straight line, in which the slope equals (-ΔH/R) and its intersection (S / R), as can be seen from **Table 9**. and **10**.

Table 9. The values of the NTP's entropy, enthalpy, and free energy.

T(K)	NTP		
	ΔH (J/mole)	ΔS (J/mole.K)	ΔG (J/mole)
298	14103	-93.1	25800.80
303			32131.30
308			34561.80
313			42992.30
318			53822.80

Table 10. The entropy, enthalpy, and free energy values for [Cu (L)₂] complexes.

T (K)	[Cu(L) ₂]		
	ΔH (J/mole)	ΔS (J/mole.K)	ΔG (J/mole)
298	610000.0	870.0	59140
303			47890
313			41430
318			34440

It can be noticed in **Tables 9.** and **10.** that decomposition processes of the (NTP) as well as its complex [Cu (L)₂] were both heat-emitting (26). However, for complexes, it has been found considerably higher compared to it for ligand, because complex stability is quite high due to the fact that they're structures. Highly stable claw toroid.

Concerning (ΔS) value, it has been noted that it was negative for (NTP) hydrolysis process whereas it has been positive for complex [Cu (L)₂] and has high values. And that is because ligand (NTP) decomposition includes its transformations to ionic groups which have the tendency of increasing solvent molecules' regularity that surround ions. Which results from the decomposition and therefore, total system (ΔS) entropy has been reduced upon the moment of the decomposition.

4. Conclusion

New ligand in present study had been Produced by reaction from 4-nitro benzoyl isothiocyanate with serine The ligand was identified through elemental micro analyses of the spectra of FTIR, C.H.N.S, UV-Vis and ¹H, ¹³C-NMR. This ligand's metal complex had been produced and identified by the FTIR, UV-Visible spectra, measurements of conductivity, atomic absorptions, and magnetic susceptibility, the suggested geometrical structure for the complex have been tetrahedral geometry except the Cu complex has square planer.

Acknowledgement

The authors thank the Department of Chemistry/ College of Education for Pure Sciences (Ibn Al-Haitham)/ University of Baghdad for approving this research.

Conflict of Interest

The authors declare that they have no conflicts of interest.

Funding

There is no funding provided for this study.

Ethical Clearance

This work has been approved by the Scientific Committee at the University of Baghdad/ College of Education for Pure Science (Ibn Al-Haitham).

References

1. Hassan SA, Lateef SM, Majeed IY. Structural, spectral and thermal studies of new bidentate Schiff base ligand type (NO) derived from mebendazole and 4-aminoantipyrine and its metal complexes and evaluation of their biological activity. RJPT. 2020; 13(6):3001-3006. <https://doi.org/10.5958/0974-360X.2020.00531.4>.
2. Salloom HK, Lateef SM, Hassan SA. Structural, spectral and thermal studies of novel tridentate Schiff base ligand type (NOO) as donor atoms derived from nalidixic acid and 4-aminoantipyrine and metal complexes and evaluation of their biological activity. JGPT. 2020; 12(2):26-36.
3. Morad FM, Elajaily MM, Ben Gweirif S. Preparation, physical characterization and antibacterial activity of Ni(II) Schiff base complex. JOSAIA. 2007; 1(1):72-78.
4. Kumar RS, Arunachalam S. DNA binding and antimicrobial studies of polymer-copper(II) complexes containing 1,10-phenanthroline and L-phenylalanine ligands. EJMECH. 2009; 44(5): 1878-1883. <https://doi.org/10.1016/j.ejmech.2008.11.001>.
5. Hassan SA, Hassan WF. Structural and spectral studies of new mixed ligand complexes for 2-amino-4-nitrophenol with some metallic ions and evaluation of their biological activities. RJPT. 2022; 15(8):3634-3640. <https://doi.org/10.52711/0974-360X.2022.00608>.
6. Sarhan BM, Fyyadh BM. Synthesis and spectroscopic studies of some metal complexes of [3-(3-(2-chloroacetyl) thioureido) pyrazine-2-carboxylic acid]. QJPS. 2017; 22(2).
7. Alwan TB, Rajab MA, Hassan SA. The effect of nanoparticle and fiber reinforcement on composites used in some applications of internal combustion engine parts. EJCHEM. 2022; 65(132):411-416. <https://doi.org/10.21608/ejchem.2022.128781.5700>
8. Alwan TB, Hassan SA. Thermodynamic studies of Cu(II) complex of new bidentate Schiff base ligand type (NO) derived from mebendazole. EJCHEM. 2023; 66(1):563-572. <https://doi.org/10.21608/ejchem.2022.128827.5703>
9. Boghaei DM, Lashanizadegan M. Template synthesis, characterization of highly unsymmetrical tetradentate Schiff base complexes of nickel(II) and copper(II). J Sci R Iran. 2000; 11(4):301-304.

10. Hassan S. A, Lateef S M. Synthesis, structural, thermal and biological studies for new Schiff base derived from Isoniazid and its complexes with metal ions. EJCHEM. 2021; 64(7):3235-3243. <https://doi.org/10.21608/ejchem.2021.42643.2861>.
11. Abbas AM, Sarhan BM. Synthesis and spectroscopic study of 3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo) propanoic acid with their metal complexes. JGPT. 2019; 11(5):495-503.
12. Über die Dissociationswärme und den Einfluss der Temperatur auf den Dissociationsgrad der Elektrolyte. Zeitschrift für physikalische Chemie. 1889; 4(1):96-116. <https://doi.org/10.1515/zpch-1889-0408>.
13. Gazi A, Sarhan BM. Synthesis and spectroscopic studies of some metal complex of (4-nitrobenzoyl) carbarmothioyl) histidine(NCH). JGPT. 2018; 10(8):33-41.
14. Hassan SA, Lateef SM, Majeed IY. Structural, spectral and thermal studies of new bidentate schiff base ligand type (NN) derived from mebendazol and 2-aminobenzothiazol and its metal complexes and evaluation of their biological activity. JGPT. 2018; 10(07):307-314.
15. Daniels F, ALberty R A. Physical chemistry, fourth edition, John Wiley and Sons. Journal of New York London. 1974; 367.
16. Alwan TB, Sahran BM, Himdan T. Synthesis and spectroscopic studies of some new metals complexes with (3R)-3-hydroxy-2-(3-(4-nitrobenzoyl) thioureido) butanoic acid. Int J Pharm Res. 2020; 12(3):1022-1026. <https://doi.org/10.31838/ijpr/2020.12.03.129>.
17. Laider, Meiser, Sanctuary. Physical Chemistry. 4th ed. Houghton Mifflin. JGPT. 2003; 11:380-385.
18. Hossain MM, Bashar MA, Khan MN, Roy PK, Ali MS, Farooque MA. Preparation, physical characterization, and antibacterial activity of Ni (II), Cu (II), Co (II), Cd (II), Zn (II), and Cr (III) Schiff base complex compounds. J Chem. 2018; 6:17-23. <https://doi.org/10.11648/j.sjc.20180602.11>.
19. Alwan TB, Sarhan BM. Synthesis and characterization of some metal complexes of [1-(4-bromo-2-methyl-phenyl)-3-(4-methoxybenzoyl)-thiourea]. JGPT. 2018; 10(08):42-49.
20. Latif I, Alwan TB, Al-Dujaili AH. Low-frequency dielectric study of PAPA-PVA-GR nanocomposites. JNN. 2012; 2(6):190-200. <https://doi.org/10.5923/j.nn.20120206.07>.
21. Al-Hashimi SM, Sarhan BM, Jarad AJ. Synthesis and identification of N-acetylglycine with some metal salts. Ibn-Al-Hatham J Pure Appl Sci. 2004; 17(2):50-54.
22. Alwan TB. Thermodynamic studies of Ni complexes with 4-nitrobenzoyl-carbarmothioyl-histidine. Int J Drug Deliv Technol. 2021; 11(4):1216-1220.
23. Hanna WA, Moeaad MM. Synthesis, characterization, and antimicrobial activity of Co (II), Ni (II), and Cu (II) complexes with new asymmetrical Schiff base ligand. Transit Met Chem. 2002; 7: 140-144. <https://doi.org/10.1023/A:1012066612090>.
24. Alwan LH, Alwan TB, Mahmoud HA. Thermodynamic study of adsorption of a mixture of Nolvadex and nanoparticle ferric oxide prepared on the surface of activated charcoal. Egypt J Chem. 2021; 64(10):5915-5918. <https://doi.org/10.21608/ejchem.2021.66722.3435>.
25. Boto A, Gallardo JA, Hernández D, Hernández R. Synthesis of unnatural amino acids from serine derivatives by β -fragmentation of primary alkoxyl radicals. J Org Chem. 2007;72(19):7260-7269. <https://doi.org/10.1021/jo071155t>.

26. Hassan SA. Synthesis and characterization of mixed ligand complexes from curcumin and new Schiff base derived from isatin for some metallic ions and evaluation of biological activities. Res J Pharm Technol. 2022; 15(4):1537-1542. <https://doi.org/10.52711/0974-360X.2022.00256>.