RESEARCH ARTICLE

Thermodynamic Studies of Ni^{+2} Complexes with 4-nitrobenzoyl-carbarmothioyl-Histidine

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ABSTRACT

In this research, the prepared ligand and its complexes were studied by studying the effect of temperature between 25 to 45°C and different concentrations on the values of molar conductivity from the application of Arinus' law, through which we determine the uniform molar conductivity and decomposition constant, thermodynamic parameters (ΔS, ΔH, and ΔG) were calculated and discussed. The results show that molar conductivity increases with increasing temperature and decreases with concentration increase through a solvent dimethylsulfoxide (DMSO). The dissociation process is exothermic process for complexes (M^{+2} = Ni).

Keywords: Histidine derivatives, Nickel Complexes, Theromdynamic measurments.

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INTRODUCTION

Amino acids are the building blocks of proteins, are indispensable because of their biological functions, as exemplified by the role of enzymes, especially[1] Histidine, contains an-amino group and acarboxylic acid group and animdazole, chain and is common coordination ligand in meallo protein and poot of catalytic sites in certain enzymes.[2,3]

Transition metal complexes of (4-nitrobenzoyl) carbamothioyl) histidin (HL) have attracted much attention as they give geometrical isomers. nickel complexes are known to assume trans structure.[4,5] The complexation of transition metals as an electron acceptor with various electron donor bases, including as an acceptor to form charge-transfer complexes has been extensively studied.[6] These complexes show interesting physical properties such as electrical conductance.[7]

In our research, the aim of this work is that molar conductivity was measured at temperatures between (25–45)°C and at different concentrations using the DMSO solvent and noting the changes and the resulting results of this work.[8]

The study showed that with increasing concentration, molar conductivity decreases. On the contrary, with increasing temperature, the conductivity will increase. By applying the Arinus equation,[9] we were able to explain the results that we reached, which are the stability of the ligand, its complexes, and the fact that they are heat-emitting.

EXPERIMENTAL

Ligand and Complexes

Ligand and its nickel complex prepared by other researchers,[10] on which all the measurements required by the researcher were made from:

- ^{1}H and ^{13}C NMR were recorded using Ultra Shield 300 MHz Switzerland at University of Al Albayt, Jordan.
- Melting point was recorded by using melting point meter KRUSS (A, KRUSS OPTRONIC).
- FT-IR spectra were recorded as FT-IR using 3800Shimadzu in the range of 4000 to 400 cm^{-1} by using (KBr) disc.
- Electronic spectra were obtained using (UV-160 Shimadzu) spectrophotometer at 25°C for 10^{-3} M Solution DMSO.
- Molar Conductivity was measured at 25°C for (10^{-3}) M by using Philips PW. That was worked on by making physical measurements represented by the thermodynamic functions (ΔS, ΔH and ΔG)

Physical Measurements

Conductivities were measured in DMSO solvents using PHILIPS PW9526 digital conductivity meter with a cell constant of 0.829 cm^{-1}. Various concentration (10^{-3}–10^{-4}) molar was measured at 25 to 45°C. Also, concentrations between (0.1–0.5) g/liter were worked out.

The molar conductivity of the ligand and its complex were measured at different concentrations values and temperatures ranging between 25 to 45°C. The specific molar conductivity

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was extracted by subtracting the solvent conductivity from the solution's conductivity.

The results found that the higher the concentration, the lower the conductivity, and vice versa to the temperature, the higher the molar conductivity increased, and thus it was concluded that it is the ligand and the complex that exothermic process.

RESULT AND DISCUSSION

A ligand and its complex, solid and stable towards air moisture, They decompose at high temperature (232–233)°C, and they are less soluble in methanol, ethanol as solvents but soluble in DMSO, As in the following Table 1.

All the metal chelates have 1:2 (metal:ligand) stoichiometry from the atomic absorption analysis.

Infrared Spectra

The fourier transform infrared spectroscopy (FTIR) spectrum of the free ligand (HL), Figure 1 shows broad band at (3116-3062) cm^{-1} due to υ(OH). While other absorption bands at (1716) ccm^{-1}, (1350)ccm^{-1}, (1604)ccm^{-1}, (1215) cm^{-1} due to υ(COO_{asy}), υ(COO_{sym}), υ(C=O amidic) and υ(C=S) respectively.[11] The FTIR spectral data of the free ligand (HL) are listed in Figure 1.

Thermodynamics Study

The Effect of Different Concentrations on Molar Conductivity

The molar conductivity values of a ligand (HL) and its complex [Ni (L)2] were obtained in the DMSO solvent at different concentrations and temperatures, and as in the Tables 2 and 3.

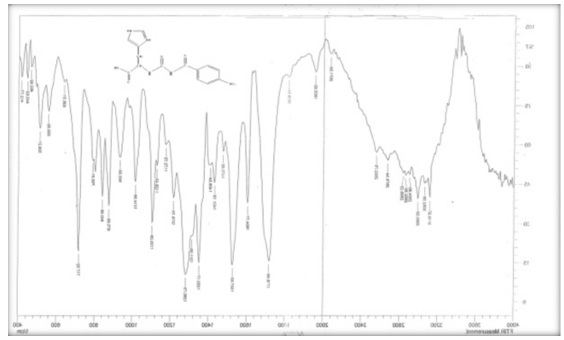

Figure 1: Infrared spectrum of ligand (HL)

Table 1: The Characteristics and analyses of the ligand and their complexes.

Compound	*M.wtt (gm/mole)*	*Color*	*M.P(°C) ordec.*	*M% calculation (Found)*	*Molar cond.ohmm^{-1}cm^{2}mol^{-1} in DMSO*	*μeff (B.M)*
Lignd (HL)	363	Brown	158–160	—	—	—
[Ni(L)2]	782.71	Yellow	232–233 Dec	(7.10) 7.50	15.4	2.99

Table 2: The conductivity values of (HL) in the solvent of (DMSO) in different concentrations and temperatures

HL					
25°C			*30°C*		
C (g/L)	*C(M)*	*S (mho)*	*C (g/L)*	*C(M)*	*S (mho)*
0.1	3.55E-04	6.72E-07	0.1	4.55E-04	1.07E-07
0.2	8.09E-04	0.36E-06	0.2	8.08E-04	0.52E-07
0.3	1.36E-03	0.74E-06	0.3	1.36E-03	2.40E-07
0.4	1.87E-03	2.07E-06	0.4	1.87E-03	2.67E-07
0.5	3.25E-03	3.34E-06	0.5	3.25E-03	3.82E-07
35°C			*40°C*		
C (g/L)	C(M)	S (mho)	C (g/L)	C(M)	S (mho)
0.1	3.55E-04	1.32E-07	0.1	3.55E-04	1.51E-07
0.2	8.09E-04	2.05E-07	0.2	8.09E-04	2.40E-07
0.3	1.36E-03	2.60E-07	0.3	1.36E-03	3.00E-07
0.4	1.87E-03	3.16E-07	0.4	1.87E-03	3.80E-07
0.5	3.25E-03	3.60E-07	0.5	3.25E-03	4.30E-07
45°C					
C (g/L)	C(M)	S (mho)			
0.1	3.55E-04	1.60E-07			
0.2	8.09E-04	2.75E-07			
0.3	1.36E-03	3.20E-07			
0.4	1.87E-03	3.95E-07			
0.5	3.25E-03	5.20E-07			

Table 3: The conductivity values of complex [Ni $(L)_2$] in DMSO solvent in different concentrations and temperatures

[Ni(L)₂]					
25°C			*30°C*		
C (g/L)	*C(M)*	*S*	*C (g/L)*	*C(M)*	*S*
0.1	1.80E-04	9.31E-08	0.1	1.80E-04	2.16E-08
0.2	3.65E-04	1.25E-07	0.2	3.65E-04	3.10E-08
0.3	5.70E-04	1.82E-07	0.3	5.70E-04	3.45E-08
0.4	8.27E-04	1.89E-07	0.4	8.27E-04	4.24E-08
0.5	9.12E-04	1.89E-07	0.5	9.12E-04	4.84E-08
35°C			*40°C*		
C (g/L)	*C(M)*	*S*	*C (g/L)*	*C(M)*	*S*
0.1	1.80E-04	4.55E-08	0.1	1.80E-04	7.40E-08
0.2	3.65E-04	6.80E-08	0.2	3.65E-04	1.32E-07
0.3	5.70E-04	8.35E-08	0.3	5.70E-04	1.81E-07
0.4	8.27E-04	1.09E-07	0.4	8.27E-04	2.01E-07
0.5	9.12E-04	1.14E-07	0.5	9.12E-04	2.40E-07
45°C					
C (g/L)	C(M)	S			
0.1	1.80E-04	9.01E-08			
0.2	3.65E-04	1.80E-07			
0.3	5.70E-04	2.45E-07			
0.4	8.27E-04	3.73E-07			
0.5	9.12E-04	4.10E-07			

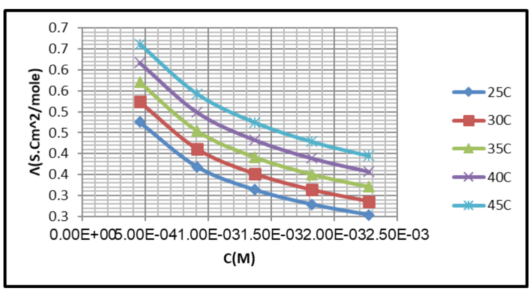

Figure 2: The decrease in the molar conductivity values of (HL) by increasing the concentration of the solution and at different temperatures.

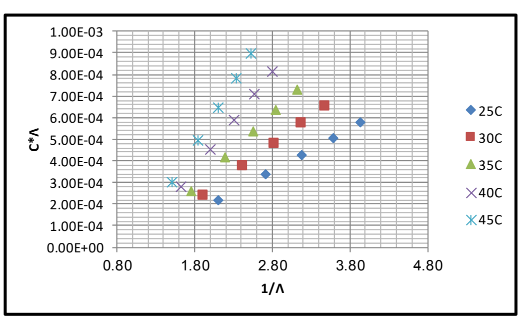

Figure 3: The relationship of concentration to the reciprocal of conductivity of a ligand (HL) with increasing solution concentrations with different temperatures

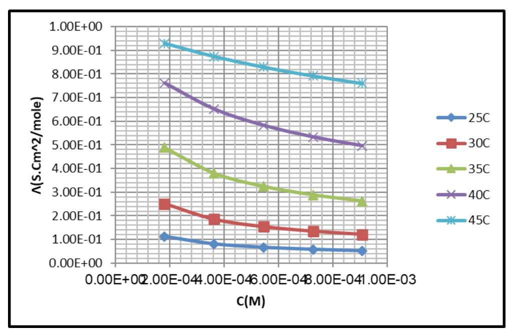

Figure 4: The decrease of the molar conductivity values of the complexes $[Ni(L)_2]$ with the increase in the concentration of the solution And at different temperatures

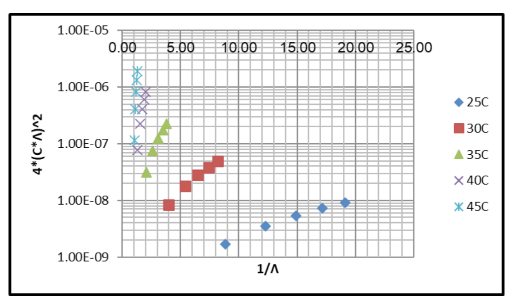

Figure 5: The relationship of concentration to the reciprocal of the molar conductivity of the complex $[Ni(L)^2]$ by increasing the concentration of the solution with different temperatures

Figure 2 to 5 shows the decrease in the value of the molar conductivity of the ligand (HL) and its complexes $[Ni(L)_2]$ the last concentrations of the natural solution in line with the behaviors of the solutions of the electrolytes poor for ligand.

The Effect of Temperature on Molar Conductivity

As for the effect of temperature on the conductivity value,[12] both systems increase the value of molar conductivity with increasing temperature, and according to what is stipulated by the Arinus relationship.[13,14] The Arinus relationship for conductivity is in the following equation:

$$e^{-Ea/RT} \quad (1)$$

The hydrolysis equilibrium constant of (HL) and its complex $[Ni(L)_2]$ were extracted through the basic relationships of dissociation and complex of the two solutions of ligand as follows:

$$HA \rightleftharpoons H^+ + A^- \quad (2)$$

C 0 0

c(1-α) αc αc

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

$$\alpha = \frac{\Lambda}{\Lambda_o} \quad (4)$$

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

And the linear form adopted for extracting the values of K_L and o for ligand was:

$$\Lambda C = \Lambda 2_O K_L \cdot (1/\Lambda) - \Lambda_O K_L \quad (6)$$

As the slope of this relationship = $\Lambda^2{}_O K_L$

And the relationship is intersected = $\Lambda_O K_L$

Where the values of these constants have been listed in Table 4**.**

As for the relationship of the complex decomposition constant $[Ni(L)_2]$,[15] it was as follows:

$$NiL_2 \rightleftharpoons Ni^{+2} + 2L^-$$

	C	0	0
C(1-α	αc	2αc	αc +αc

$$K_{coplx} = \frac{4\alpha^3 C^3}{C(1-\alpha)} = \frac{4\alpha^3 C^2}{(1-\alpha)} \quad (7)$$

$$K_{coplx} = \frac{4(\frac{\Lambda}{\Lambda_o})^3 C^2}{1-\frac{\Lambda}{\Lambda_o}} \cdot (\frac{\Lambda_o}{\Lambda_o})^3 \quad (8)$$

Table 4: The specific molar conductivity values Λ_O and the arinus constant for each of the ligand (HL) and its complexes $[Ni(L)_2]$ at absolute temperature.

	HL		*Ni(L)₂*	
T(K)	*K*	*Λ0*	*K*	*Λ0*
298	2.96457E-06	93.626	9.2E-08	40.572
303	2.89825E-06	70.510	3.43E-07	45.213
308	3.14254E-06	114.524	1.23E-06	58.743
313	3.26742E-06	144.105	5.25E-06	82.788
318	3.6239E-06	181.730	1.8E-05	120.423

$$K_{coplx} = \frac{4\Lambda^3 C^2}{\Lambda_o^3 - \Lambda\Lambda_o^2} \quad (9)$$

$$4(\Lambda C)^2 = (K_{coplx}\Lambda_o^3 (\frac{1}{\Lambda}) - K_{coplx}\Lambda_o^2) \quad (10)$$

The last equation is the linear form of the $[Ni(L)_2]$ decomposition relationship, whereby plotting 4 $(\Lambda C)^2$ on the y-axis (Y) versus ((1/Λ)) on the x-transformer (X), we get a straight line that is

Slope = $K_{coplx}\Lambda_o^3$

Intersection = $K_{coplx}\Lambda_o^2$

Thus, the values of (Λ_o) and the complex decomposition constant were extracted from where the values were included in table 4.

We note in Table 4 that the values of (Λo) for HL are low in general and especially by comparing them with the values of (Λo) for the weak electrolytes in aqueous solutions due to the transport mechanism of the dissolved proton in DMSO that is not compatible with the proton transport mechanism. In aqueous solutions, the value of the specific molar connections (Λo) of the lycand solution HL and at various temperatures is greater than that of the complex $[Ni(L)_2]$ and this is due to the reason that:

Although the value of the specific molar conductivity (Λo) of the proton is low (due to the difference of the solvent), it remains high compared to other ions due to the small size of the proton and its small mass (low intrinsic inertia). Therefore, the specific molar conductivity (Λo) of ligand solutions HL is considered a weak acid. It is larger than that of $[Ni(L)_2]$ complexes.

Concerning the values of the constants of HL and its complex $[Ni(L)_2]$, we notice that in the case of ligand (HL) they are within the normal limits of the weak acid dissolution constants and the difference of the solvent did not change this nature due to the considered polarity of the substance DMSO.

As for complexes $[Ni(L)_2]$, although it has low values, it is considered high compared with the corresponding decomposition constants in aqueous solutions.

Thermodynamic Functions

The thermodynamic functions-16 of the degradation of ligand (HL) and its complex $[Ni(L)_2]$ were extracted through the following basic relationships:

$$\Delta G = -RT \ln K \quad (11)$$

$$\ln K = (-\Delta H/R) * (1/T) + (\Delta S/R) \quad (12)$$

Whereas, by plotting the relationship No. (12) (LnK) versus (1/T), we get a straight line whose slope is (-ΔH/R) and its intersection (S/R), as shown in Table 5.

Where we notice in Tables 5 and 6 that both the decomposition processes of HL and its complex $[Ni(L)_2]$ are heat-emitting.[17] But for the complexes, it is much higher than for the ligand because the stability of the complexes is very high because they are structures of highly stable claw toroid.

Table 5: The values of enthalpy, entropy, and free energy of (HL).

	HL		
T(K)	*ΔH(J/mole)*	*ΔS(J/mole.K)*	*ΔG(J/mole)*
298	10103.00	-53.100	21800.8
303			22131.3
308			22461.8
313			22792.3
318			43122.8

Table 6: The values of enthalpy, entropy and free energy for complexes [Ni (L)2]

	[Ni(L)2]		
T	*ΔH(J/mole)*	*ΔS(J/mole.K)*	*ΔG(J/mole)*
298	310000.00	670.000	50140
303			47290
308			44440
313			41590
318			32740

As for the value of (ΔS), we note that it is negative for the hydrolysis process of HL while it is positive for the complexes $[Ni(L)_2]$ and has a high value (Table 6). This is because the decomposition of the ligand (HL) includes its transformation into ionic groups that tend to increase the regularity of the solvent molecules around the ions. Resulting from decomposition and thus the total entropy of the system (ΔS) is reduced upon decomposition.

CONCLUSIONS

As demonstrated by looking at the research and depending on the results obtained molar conductivity from the application of Arinus' law, thermodynamic parameters (ΔS, ΔH and ΔG), magnetic moment, spectroscopic studies (FTIR, UV-Vis and atomic absorption for the ligand (HL) and all prepared complexes $[Ni(L)_2]$ add too(^{1}H-^{13}C-NMR) only for ligand, we conclude the following:

- The results show that molar conductivity increases with increasing temperature and decreases with concentration increase using solvent (DMSO).
- In the future we can study ligand and complex biology.
- In the future we can mix nanomaterials with both ligand and complexes to see the change that will get the results.

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