American Journal of Chemistry 2012, 2(2): 23-26
DOI: 10.5923/j.chemistry.20120202.05

The Association and Formation Constants for $CuCl_2$ Stoichiometric Complexes with (*E*)-3-(2-Benzylidene Hydrazinyl)-3-oxo-N-(thiazol-2-yl)Propanamide in Absolute Ethanol Solution at 294.15 K

Kamal M. Ibrahim[*], **Esam A.Gomaa**, **Rania R. Zaky**, **Mahmoud N. Abdel El-Hady**

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

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Abstract The association constants and Gibbs free energies for $CuCl_2$ with (*E*)-3-(2-benzylidene hydrazinyl)-3-oxo-N-(thiazol-2-yl)propanamide (H_2BH) had been calculated by using the conductometric titration curves in absolute ethanol at 294.15 K. New equation was applied to determine the association constant for 1:2 asymmetric salts. Different stoichiometric complexes were obtained on drawing the relation between (Λ_m) and (*M:L*). The association free energies that were evaluated for $CuCl_2$-ligand complexes were small and spontaneous indicating electrostatic attraction force. The formation constants and Gibbs free energies of different complexes follow that order: K_f (2:1) › K_f (1:1) › K_f (1:2) for (M:L), and ΔG_f (2:1) › ΔG_f (1:1) › ΔG_f (1:2) for (M:L).

Keywords Association Constants, Formation Constants, Gibbs Free Energies, Stoichiometric Complexes, Copper Chloride , Benzylidene Hydazinyl Propanamide

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1. Introduction

Recently, there has been growing interest in the development of ligands that are able to effectively and selectively bind metal ions through multiple non-covalent interactions[1]. Iron, copper and zinc from ions which involved in metalloproteins. For example, metallo-enzymes belong to a subclass of metalloproteinase which perform a specific catalytic function. There are three known classes of dioxygen transport proteins involved in respiration: the haemoglobin- myoglobin family, haemocyanines and hemerythrins. These metal ions may differ from one organism to another[1], The concentrations of metal ions are very important for the normal function of biological systems. An excess of Cu(II) and Fe(II) may include thalaseamia disease[1].

The aim of this work the evaluation the non-covalent behaviour of $CuCl_2$ with (*E*)-3-(2-benzylidene hydrazinyl)-3-oxo-N-(thiazol-2-yl)propanamide (H_2BH) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environnement[1]. Evaluation of individual ionic molar volumes[2], preferential salvation of drugs[3] partial molar volumes[4], ligands used for selective metal extraction [5], ionic solvation[6], potntiometric study [7] and specific solvation [8] are some trends of this area of physical inorganic chemistry.

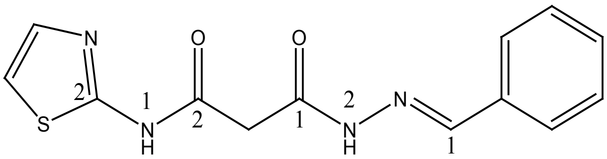
2. Experimental

2.1. Material and Methods

All manipulations were performed under aerobic conditions. The copper chloride salt and absolute ethanol used were pure (Merck).

2.2. Preparation of the Ligand

(*E*)-3-(2-benzylidene hydrazinyl)-3-oxo-N-(thiazol-2-yl) propanamide (H_2BH) (Structure 1) was prepared by heating a mixture of 3-hydrazinyl-oxo-N-(thiazole-2-) propanamide (0.01 mol; 2.00 g) and benzaldehyde (0.01 mol; 1.06 g) under reflux in absolute ethanol for 3 h. On heating, white crystals were formed, filtered off, washed and recrystallized from absolute ethanol (M.P.: 230 °C; yield 80%). The purity of the compound was checked by TLC.



Structure 1. (*E*)-3-(2-benzylidenehydrazinyl) - 3-oxo – *N* - (thiazol-2-yl) propanamide

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[*] Corresponding author:
kamibraim@mans.edu.eg (K.M. Ibrahim)

The conductometric titration of the ligand (1x10^{-4}) mole/L against $CuCl_2$ (1x10^{-4}) mole/L in absolute ethanol was performed with 0.5 ml interval additions from $CuCl_2$ solution, as explained in previous papers[9-11]. The specific conductance values were recorded using conductivity bridge HANNA, H1 8819N with a cell constant equal to one. The conductometer was connected to ultra thermostat of the type Kottermann 4130. The temperature was adjusted at 294.15 K.

3. Results and Discussion

The specific conductance values (K_s) of different concentrations of $CuCl_2$ in absolute ethanol were measured experimentally in absence and presence of ligand at 294.15 K. From the specific conductance, the molar conductance (Λ_m) were calculated by using equation (1)[12]:

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \qquad (1)$$

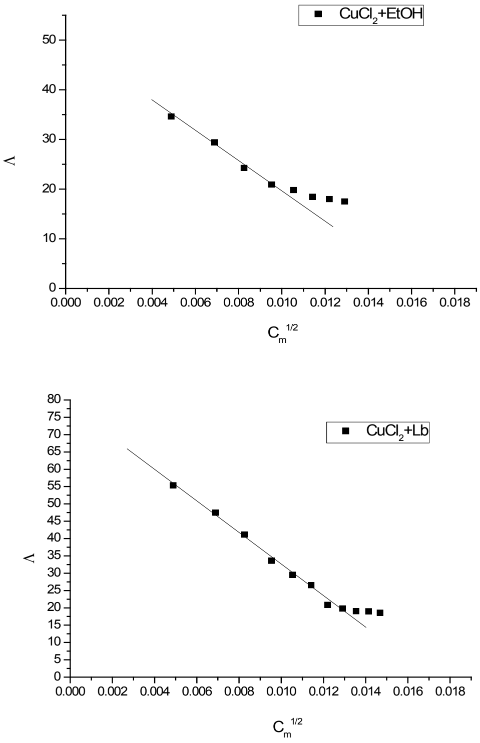


Figure 1. The relation between molar conductance (Λ_M) and ($\sqrt{C}$) of (A) $CuCl_2$ alone and (B) in presence of ligand in absolute ethanol at 294.15 K

Where (K_s) and (K_{solv}) are the specific conductance of solution and solvent, respectively; (K_{cell}) is the cell constant and (C) is the molar concentration of the $CuCl_2$ solutions. The limiting molar conductance (Λ_o) at infinite dilutions were estimated for $CuCl_2$ in absolute ethanol in absence and presence of the ligand (H_2BH), by extrapolating the relation between (Λ_m) and ($C_m^{1/2}$) to zero concentration (Fig. 1). By drawing the relation between molar conductance (Λ_m) and the molar ratio of metal to ligand concentrations, different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1 ($M:L$) stoichiometric complexes (Fig. 2).

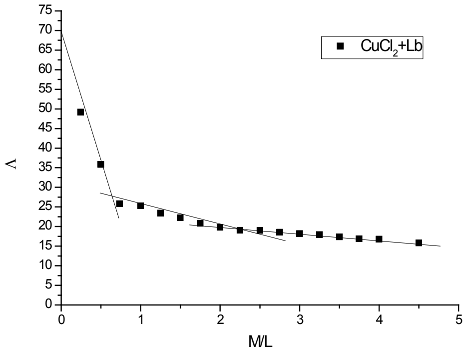


Figure 2. The relation between molar conductance (Λ_M) and the molar ratio (M/L) of $CuCl_2$ in the presence of ligand in absolute ethanol at 294.15 K

The experimental data of (Λ_m) and (Λ_o) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes. The association constants of $CuCl_2$ in the presence of ligand (H_2BH) in absolute ethanol at 294.15 K for 1:2 asymmetric electrolytes were calculated by using equation (2)[13, 14].

$$K_A = \frac{\Lambda_0^2(\Lambda_0 - \Lambda_m)}{4C_m^2 + \Lambda^3 S(z)} \qquad (2)$$

Where (Λ_m, Λ_0) are the molar and limiting molar conductance of $CuCl_2$; (C_m) is molar Concentration of $CuCl_2$ and S (Z) is Fuoss-Shedlovsky factor and equal approximately one for strong electrolytes[15]. The calculated association constants are shown in Table 1. The Gibbs free energies of association (ΔG_A) were calculated from the association constant[15,16] by applying equation (3):

$$R\,T \ln KA = -\Delta\, GA \qquad (3)$$

Where (R) is the gas constant (8.341 J) and (T) is the absolute temperature (294.15 K). The calculated Gibbs free energies were presented in Table 1.

Table 1. Association constants and Gibbs free energies of association for $CuCl_2$ with H_2BH in absolute ethanol at 294.15 K

Λ_m ($cm^2.Ohm^{-1}$)	C	Λ_o $-\Lambda_m$	$\Lambda_o^{\ 2}$ $(\Lambda_o-\Lambda_m)$	$4C^2+\Lambda^3_m$	K_A	Δ G_A(k J/mol)
49.20	2.439×10^{-5}	29.8	1.859×10^{5}	1.191×10^{5}	1.562	-1.089
31.50	4.762×10^{-5}	47.5	2.964×10^{5}	3.126×10^{4}	9.484	-5.499
25.80	6.977×10^{-5}	53.2	3.304×10^{5}	1.717×10^{4}	19.334	-7.241
25.30	9.091×10^{-5}	53.5	3.339×10^{5}	1.619×10^{4}	20.619	-7.398
23.402	1.111×10^{-4}	55.59	3.469×10^{5}	1.282×10^{4}	27.075	-8.064

Λ_o = 79 $cm^2.Ohm^{-1}$

Table 2. Formation constants and Gibbs free energies of formation for 1:2 (M/L) $CuCl_2$-H_2BH complexes in ethanol at 294.15 K

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	(Λ_{obs}-Λ_{ML})[L]	(Λ_M-Λ_{obs})	K_f	Δ G_f (k J/mol)
49.2	9.756×10^{-5}	2.361×10^{-3}	1.8	7.6242×10^{3}	-16.224
31.5	9.523×10^{-5}	6.189×10^{-4}	19.5	3.150×10^{4}	-25.322
25.8	9.302×10^{-5}	7.442×10^{-5}	25.2	3.386×10^{5}	-31.128

ΛM = 51 cm2.Ohm-1 , ΛML = 25 cm2.Ohm-1

Table 3. Formation constants and Gibbs free energies of formation for 1:1 (M/L) $CuCl_2$- H_2BH complexes in ethanol at 294.15 K

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	(Λ_{obs}-Λ_{ML})[L]	(Λ_M-Λ_{obs})	K_f	Δ G_f (k J/mol)
25.3	9.091×10^{-5}	5.727×10^{-4}	25.7	4.487×10^{4}	-26.187
23.4	8.888×10^{-5}	3.911×10^{-4}	27.6	7.058×10^{4}	-27.294
22.234	8.696×10^{-5}	1.017×10^{-4}	28.766	2.827×10^{4}	-30.686
20.819	8.511×10^{-5}	1.548×10^{-4}	30.181	1.949×10^{5}	-29.778
19.807	8.333×10^{-5}	6.733×10^{-4}	31.193	4.633×10^{5}	-31.894

$\Lambda_M = 51\ cm^2.Ohm^{-1}$, $\Lambda_{ML} = 16.5\ cm^2.Ohm^{-1}$

Table 4. Formation constants and Gibbs free energies of formation for 2:1 (M/L) $CuCl_2$- H_2BH complexes in ethanol at 294.15 K

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	(Λ_{obs}-Λ_{ML})[L]	(Λ_M-Λ_{obs})	K_f	Δ G_f(k J/mol)
19.055	8.163×10^{-5}	2.086×10^{-4}	31.945	1.532×10^{5}	-29.187
19.000	8.000×10^{-5}	2.00×10^{-4}	32.000	1.600×10^{5}	-29.294
18.547	7.843×10^{-5}	1.605×10^{-5}	32.453	2.022×10^{5}	-29.867
18.201	7.692×10^{-5}	1.307×10^{-4}	32.800	2.508×10^{5}	-30.394
17.938	7.547×10^{-5}	1.085×10^{-4}	33.062	3.047×10^{5}	-30.869
17.358	7.407×10^{-5}	6.356×10^{-5}	33.642	5.293×10^{5}	-32.220

$\Lambda_M = 51\ cm^2.Ohm^{-1}$, $\Lambda_{ML} = 16.5\ cm^2.Ohm^{-1}$

The formation constants (K_f) for $CuCl_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using equation (4)[17, 18]:

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (4)$$

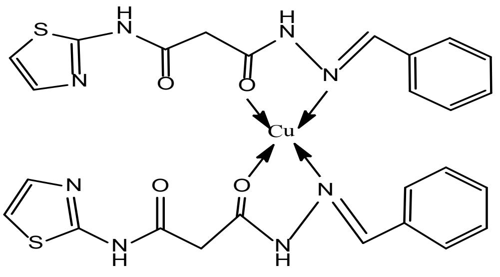
Where (Λ_m) is the molar conductance of the $CuCl_2$ before addition of the ligand, (Λ_{obs}) is the molar conductance of solution during titration and (Λ_{ML}) is the molar conductance of the complex.

The obtained values (K_f) for $CuCl_2$-ligand stoichiometric complexes are represented in Table 2-4. Also the Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation (5):

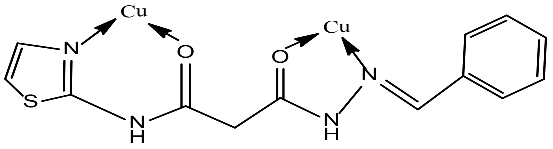
$$\Delta G_f = R\ T\ \ln K_f \qquad (5)$$

The calculated ΔG_f values are represented in Tables 2-4. The association free energies evaluated for $CuCl_2$-ligand complexes are small and spontaneous indicating electrostatic attraction force. The formation constants and Gibbs free energies of different complexes in absolute ethanol at 294.15 K follow that order: K_f (2:1) › K_f (1:1) › K_f (1:2) for (M:L), and ΔG_f(2:1) › ΔG_f(1:1) › ΔG_f(1:2) for (M:L).

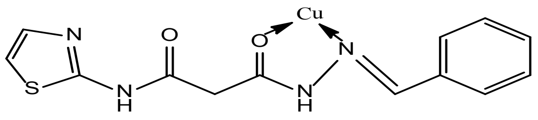
The formation of 2:1, 1:1 and 1:2 complexes indicate that H_2BH acts as flexi dentate ligand (Structures 2-4).



Structure 2: 1:2 ($Cu:H_2BH$)



Structure 3: 2:1 ($Cu:H_2BH$)



Structure 4: 1:1 ($Cu:H_2BH$)

4. Conclusions

In this paper, the association constants, the formation constants and Gibbs free energies for $CuCl_2$ with (H_2BH) had been calculated. The association free energies evaluated for $CuCl_2$-ligand complexes are small and spontaneous indicating electrostatic attraction force. While, The formation constants and Gibbs free energies of different complexes follow that order: $K_f(2:1) › K_f(1:1) › K_f(1:2)$ for (M:L), and $\Delta G_f(2:1) › \Delta G_f(1:1) › \Delta G_f(1:2)$ for (M:L)

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