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Research Article

Synthesis and Study of Complexation reaction of a newly synthesized Ligand ((*E*)-1-(2-hydroxybenzylidene)-4-phenylthiosemicabazide) with some Transition Metal Ions in Acetonitrile Solution

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Abstract: The synthesis and Complexation properties of a new substituted coumarin derivetive, towards certain transition metal ions, (M, where M = Ni, cd, Zn, Cu) in acetonitrile has been reported in this work. The stoichiometries of complexes were determined using UV- Visible spectroscopy studies. The stability constants of complexes were influenced by parameters such as the type of metal, ligand, counter ion or solvent. The formation constants of the complexes were determined for the synthesized ligand with several metallic cations, in acetonitrile solution by UV - Visible spectrometry.

Keywords: Complexation, job's method (*E*)-1-(2-hydroxybenzylidene) phenylthiosemicabazide; Spectrophotometry.

INTRODUCTION

The synthesis and metal complex structures of substituted triazole ligands have gained considerable attention in recent years[1-5].

Coumarin and its derivatives are used as additives in food, perfumes, cosmetics, pharmaceuticals, agrochemicals [6, 7], for their spasmolytic, cardiothioc, antiviral, anticancer properties[8,9] and as laser dyes in the blue- green region. These types of dyes have been employed as labels for fluorescent energy transfer experiments [10, 11]. Coumarin compounds also form a group of more than 40 drugs, which are

widely used in medicines as anticoagulant, hypertensive, ant arrhythmic and immunomodulant agents[12]. Many coumarins were tested for various kinds of biological activity and their structures established based on chemical analytical techniques and spectroscopic methods[13-18]

Substituted triazoles have been actively studied as bringing ligands toward transition metal ions coordinating through their N atoms[5]. The complexes of triazols are good candidates for the construction of various ligand metal coordination polymers[19-23].
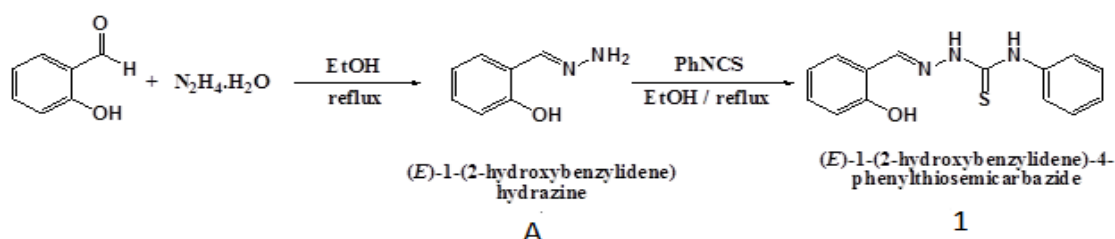
Traditionally, In order to study the complexation of new synthesized ligand with metallic cations, potentiometry, paper electro-phoresis, membrane permeation, affinity capillary electrophoresis, UV- Vis and fluorescence spectroscopy, and mass spectrometry can be used[24-27]. In this study, UV- Vis spectroscopy was chosen because of its simplicity, low cost and availability of the UV- Visible spectrophotometer in most laboratories. In this work the complexation behavior of a newly synthesized ligand L with selected metallic cations have been studied and the stoichiometry and formation constants of the complexes of the synthesized ligand, with several metallic cations in acetonitrile solvent were determined by UV- Visible spectroscopy which was established by NMR and IR spectroscopes.

EXPERIMENTAL

Materials and Methods: All reagents were of analytical grade, and all solvents were commercially available (from Merck) and used with no further purification. All UV- Visible Studies were carried out on a computerized WPA- Biowave II instrument using a l0 mm quartz cell. IR spectra were obtained using a nexus 670 FT- IR Thermo Nicolet spectrometer using KBr disk. 'H NMR spectra were recorded on 300 MHZ NMR Instrument using TMS as an internal standard in $CDCl_3$. The melting point was determined on an electro thermaldigital melting point apparatus and was uncorrected.

For synthesizing ligand (A): a solution of salicylaldehyde (3 mmol) in absolute ethanol (20 mL) was added to hydrazinehydrate (3 mmol). The resulting mixture was refluxed for 6 h. After cooling at room temperature, the solid product formed was separated by filtration, washed with diethyl ether and purified by crystallization from ethanol.

For synthesizing a ligand **L** (**1**): a mixture of compound A (1 mmol) and phenyl isothiocyanate (1 mmol) in ethanol (25 mL) was refluxed on a water bath for 6 h. The resulting solution was cooled and the solid was crystallized and separated from ethanol. Yield: 76% MP: 192-196°c. IR (KBr, cm^{-1}): 3 438.8, 3162.8, 3052.1, 3006.3, 2925.8, 2900.7, 2868.4, 2725.1, 2581.7, 1941.4, 1797.9, 1633.2, 1576.2, 1496.3, 1458.4, 1414.4, 1374.7 1246.2, 1202.8, 1148.5, 110.2, 1041.0, 1019.2, 977.0, 855.7, 750.2, 646.4, 558.4, 474.7 ; 'HNMR (300 MHz, $CDCl_3$): 6.8-6.88(2H, m, ArH), 7.15-7.24 (2H, m, ArH), 7.35 (2H, t, J=7.5, ArH), 7.55 (2H, d, J=7.5, ArH), 8.07 (1H, d, J=7.5, ArH), 8.47 (1H, s, CH=N), 9.96 (1H, s, OH), 10.03 (1H, s, NH), 11.75 (1H, s, NH).

Scheme-1:Synthesis rout of ligand (L).

Complex Formation: All solutions were prepared using acetonitrile. Small volumes of concentrated metal cation solutions (e.g. 0–100 μl from stock solutions with a concentration of 10^{-3}M) were added to ligand solution(s) 2 mL of a 5×10^{-5}M stock solution). The solutions were thermo stated at 25°c. Examples of the changes in absorbonce due to complex formation is given in Figure1 for Ni(II), and **Figure2** for Zn(II).

These figures clearly show the complexation of M with Ligand. Scheme 1 represents two possible structure of M in complex with L, in both ML and ML_2 types.
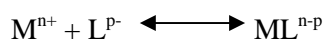

Scheme-2: Possible structure of M^{2+} complex with L,   (a) ML_2 and   (b) ML types

The stoichiometries of complexes were found using Absorbance/moleratio data, and established also using job method, the continuous variation was employed, between standard solutions of (10^{-3} M) of metal ion with the ligand (10^{-3}M) solution.

A series of solutions were prepared in which the total volume is 2 mL, with different moleratios, (eg. 0-1).Thus, the formation constants of the resulting complexes in each case were determined using the absorbance- mole ratio data by a non- linear least squares curve fitting program, KINFIT [28].

RESULTS AND DISCUSSION

For the case of simple ML complex formation, the following equation could be derived using ligand concentrations.

$M^{n+} + L^{p-} \longleftrightarrow ML^{n-p}$

$K_f = [ML^{n-p}]/[M^{n+}][L^{p-}]$

$C_L = [ML^{n-p}]+[L^{p-}]$

And $C_M = [ML^{n-p}]+[M^{n+}]$

Where C_L is total ligand and C_M is total metal concentration

$K_f [L]^2 + (1+Kf(C_M - C_L))[L] - C_L = 0$

In addition, in the case of one step ML_2 complex formation, the following equation could be derived in similar way[3].

$M + 2L \longleftrightarrow ML_2$

$K_f = [ML_2] / [L]^2 [M]$

$C_L = [L] +2 [ML_2] \quad C_M = [M^{n+}]+ [ML_2]$

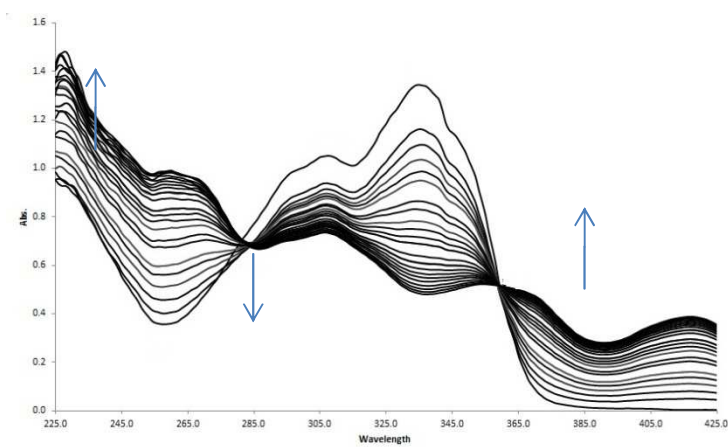$K_f [L]^3 + (2 Cm - C_L) K_f [L]^2 + [L] - C_L = 0$

Fig.1: Electronic absorption spectra of the ligand, L (10^{-3}M) in the presence of increasing amounts of Ni^{2+}ions (25°C & acetonitrile solution). [Ni^{2+}]/ [L] Mole ratios are: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3

As it is obvious from **Figure 2**, the ligand solution has strong absorption bond at 340 nm and a weaker and broader absorption at about 310 nm. The Ni^{2+} ion solution just has on absorption bond at about 210 nm. The appearance of new absorption bonds above the 370, 420 nm spectral regions, decrease in absorption at 310, and 340 nm upon mixing of two reactants in acetonitrile solution must be associated with formation of complex in solution.

Furthermore, the existence of two obvious isosbestic points at 283 and 356 nm clearly established the formation of simple ML type complex formation in the solution.
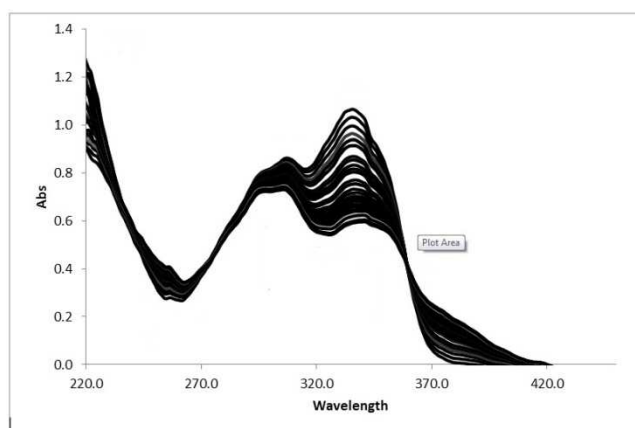

Fig.2: Electronic absorption spectra of the ligand, L (10^{-3}M) in the presence of increasing amounts of Zn^{2+}ions (25°C & acetonitrile solution). [Zn^{2+}]/ [L] Mole ratios are: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3

But in the case of Zn^{2+} the appearance of new weak absorption bond about the 380 nm spectral region and increase in the 250 nm region and from the otherwise decrease in absorption at 334and 307 nm upon mixing of two reactants in acetonitrile solution shows the formation of complex in solution. Appearance of obvious isosbestic point at 359 nm clearly is in agreement with simple one step complex formation reaction.
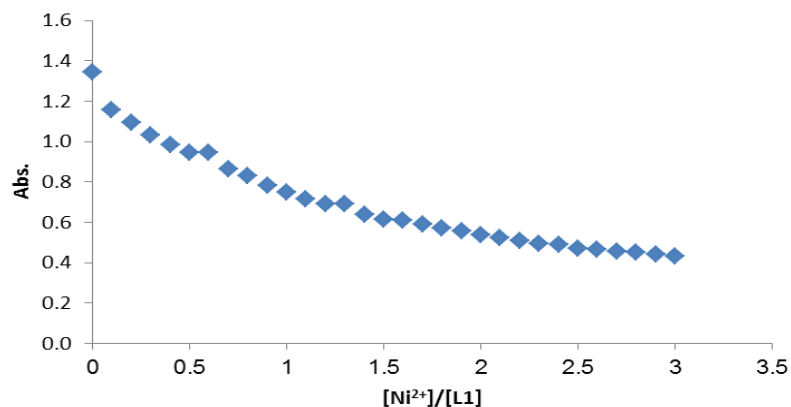

Figure-3: The corresponding abs. vs. $[Ni^{2+}]/[L]$ at 334 nm. The $[Ni^{2+}]/[L]$ mole ratio are: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.
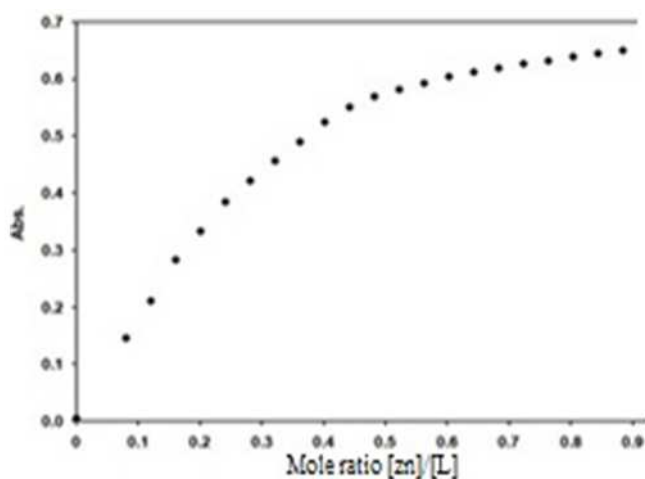

Fig.4: The corresponding abs. vs. $[Zn^{2+}]/[L]$ at 262 nm. mole ratio of $[Zn^{2+}]/[L]$ mole ratio are: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2.

The Absorbance- mole ratio plots show the stoichiometry of M-L as 1:1 in some cases and 1:2 in the others. **Figures 3** and **4.** The job's method of continuous variation results, which is completely in support of that, mentioned above shown in **Figures 5** and **6.**
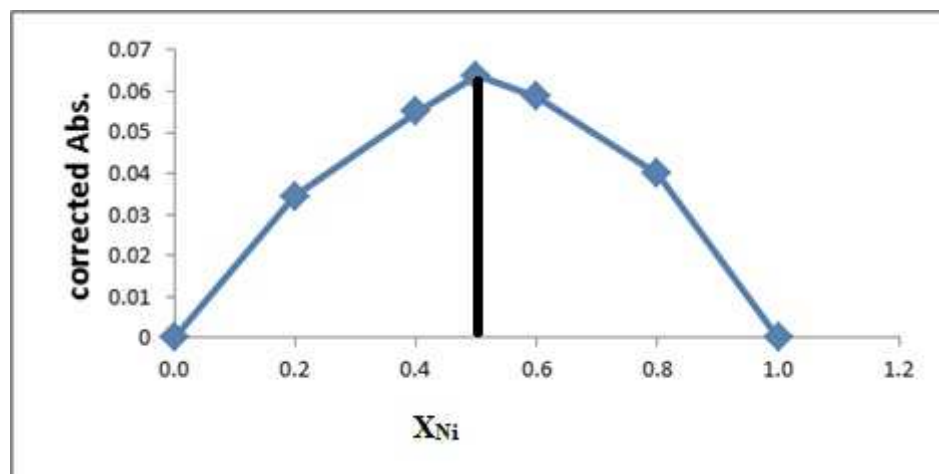

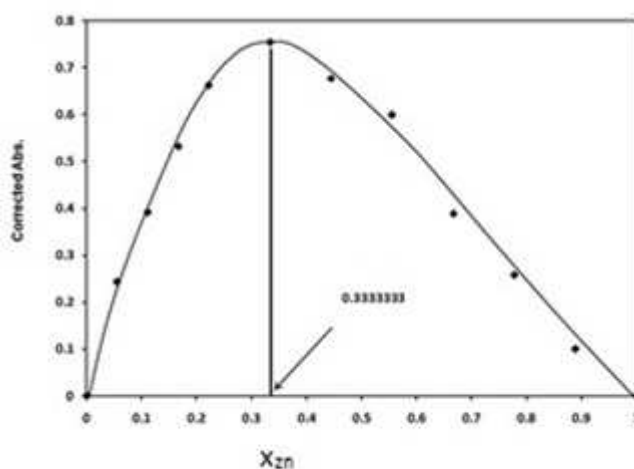**Fig.5**: **Continuous variation plot for L-Ni^{2+} system in acetonitrile solutio**n.

Fig.6: Continuous variation plot for L-Zn^{2+} system in acetonitrile solution.

In order to evaluate further the stoichiometry of M-L complex in acetonitrile solution and hopefully obtain some information about the solution structure of the resulting complex, NMR spectra of ligand before, and after adding appropriate amounts of metal ions solution, with 1:1 and 1:2 mole ratios were recorded, the resulting data are not included.

The L-M complex in crystalline form was prepared by dissolving measured amounts of Ligand and metal ions in acetonitrile. The resulting solution was then filtered and transferred into crystallization dish. The solutions were allowed to evaporate during about 24 h. the resulting crystalline crystal were

collected and dried under vacuum. The IR spectra of L and its isolated solid complex were recorded and the resulting data are included in **Table 1**.

Table-1: Formation constant values for ligand-metal complexes in acetonitrile at 25 °C.
(s=strong, b=broad)

	Functional Group	Resulting data of main IR frequencies				
Specie		L	L-Ni^{2+}	L-Cd^{2+}	L-Cu^{2+}	L-Zn^{2+}
Wavenumber (cm^{-1})	Ar-O	1247	1207	1203	1110	1031
Peak Description		s	s	S	s	s
Wavenumber (cm^{-1})	N-H	3439	3417	3421	3427	3424
Peak Description		s &b	s &b	s &b	s &b	s &b

In order to calculate the stability constants, the absorbance – mole ratio data was used by a non–linear least square, curve fitting program and the resulting data are shown in table 2.

Table-2: Formation constant values for Ligand -metal complexes in acetonitrile at 25 °C.

Parameter	Ni^{2+}	Cd^{2+}	Cu^{2+}	Zn^{2+}
Stiochiometry	ML	ML$_2$	ML	M L$_2$
pK$_f$	5.68	3.48 -2.93	6.35	4.24-2.36

CONCLUSION

In this work, the synthesis and complexation properties of a new compound, L (E) – 1 – [2- hydroxyl benzyl idien amino) ethyl] -3-has been reported towards certain transition metal ions, M (where M = zn, cu, Cd, Ni) in acetonitrile. The KINFIT program which was applied to UV- Visible spectroscopy data obtained from monitoring the reaction between L and the selected metal ions was used to determine the stoichiometry of each specie and the corresponding stability constant(s) of the complex (es). Among the tested metallic cations, Cu (II), and Ni (II), were formed the most stable complexes with this ligand. The stability of complexes were found to be respectively: Cu > Ni >Zn > Cd. Based on the results of this study the new synthesized ligand is introduced as a new active emissive probe to detect Ni (II) and Cd (II) by absorption spectroscopy either directly or after pre concentration.

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