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Research Article

Synthesis and spectrophotometric study of complexation of Cu (II) with 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amine in Acetonitrile Solution

Samadi Naser[1*], Azizi Heydarloo Sara[2]

[1]Department of chemistry, faculty of science, Urmia, Iran

[2]Department of Chemistry, Faculty of Science, Payame Noor, University (PNU), Urmia, Iran.

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ABSTRACT

With respect to specious application of phenyl hydrazine and its derivative in organic Chemistry, Pharmacy and chemical industry. On its toxicity and biological effects, the 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl amine are raised from interaction between 2-phenyl hydrazine and ceton in acid media. The constitution of this ligand is described below: presence of acetonitrile solvent in spectrophotometry the temperature is 25^{o}C method using SHIMADZU 2550 devise a complex constitution is observed by strewing $Cu^{2+}$the cation by a 10 microlitric syringe on a solvent made in a quartz cell (1cm), (that ligand with concentration of 5.8×10^{-4}). This observation was using the molar proportions. for more confidence they used other ways such as jab method with stochiometric 1:1 and spectrum method FT-IR, FT-NMR that the devices names called SHIMADZU IR470, BRUKER 200 MHZ.

Keywords: Job's method, Spectrophotometry, 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin.

INTRODUCTION:

Heavy-metal ion is ubiquitous in nature, thus resulting in a serious environment problem. Due to their high toxicity, there is an obvious need to determine them rapidly on site at trace levels. Therefore some typical detection methods such as atomic absorption spectrometry, conductometric Biosensor Based on Sol-Gel and inductively coupled plasma mass spectrometry have been use for the determination of heavy-metal ions[1].Metal ions are not only valuable intermediates in metal extraction, but are also important raw materials for technique applications. According, complexation of metal ions is an important technique for recovering metals from various sources (hydrometallurgy) and for the removal of metal ions from solutions in municipal and industrial waste. As a consequence, complexation, separation, and removal of metal ions have become increasingly attractive areas of research and have led to new technological approaches [2].

Theorems and its derivatives are useful as anti-tumor, anti-fungi, anti-bacteria, insecticidal, herbicidal, pesticide agents, and plant-growth regulators [3].Ruthenium (III) complexes containing these ligands have recently been used as catalysts for oxidation of alcohols to carbonyl compounds [4].

Traditionally, in order to study the complexation of new synthesized ligands with metallic cations; potentiometry, paper electrophoresis, membrane permeation, affinity capillary electrophoresis and UV-Vis spectroscopy was chosen because of its simplicity, low cost and availability of the UV-Visible spectrophotometer in most laboratories [5-10]. So up present, a large number of papers have been devoted to the study of complexation reaction between metal ions and various ligands.

Spectrophotometric methods are in general highly sensitive and suitable method for studying chemical equilibrium in solution.

In this work the complexation behavior of a newly synthesized theorem derivative ligand with selected metallic cation have been studied and the stoichiometry and formation constancy of the complexes of the synthesized ligand, with several metallic cation in acetonitrile solvent were determined by UV-Visible spectrophotometric studies which was established by NMR and IR spectroscopy

Experimental

Instruments

All UV-Vis studies were carried out on a Shimadzu 2250 UV-Vis spectrophotometer using a 10 mm quartz cell. IR spectra were obtained using a nexus 670 FT-IR Thermo Nicolet spectrometer using KBr disk. HNMR spectra were

*Corresponding author: Samadi Naser | E-mail: Alanin44@yahoo.com

recorded on 300 MHz NMR instrument using as an internal standard in CDCL3.

Reagents

All solvent and chemicals used in this work were of analytical grade obtained from Merck (Germany) and used with no further purification. The theorem derivative ligand, 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin was synthesized and purified.

Procedure

Firstly the absorption spectra of the ligand 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin, recorded in the wavelength range from 190 to 700 nm. Then small volumes of concentrated metal cation solutions (e.g. 0-100 from stock solutions with a concentration of 10^{-3}M) were added to ligand solution (2ml of a 5.8×10^{-4} M stock solution). The absorption spectra of the metal ion 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin complex record in the wavelength range from 200 to 700 nm and resulting changes in absorption spectra were recorded. This procedure were done for metal ion such as Cu (II). Examples of the changes in absorbance due to complex formation is given in fig.1 for Cu (II). These figures clearly show the complexation of M with 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin, Scheme 1 represents structure of M in complex with L in ML type complex.

The stoichiometry of complexes was found using absorbance mole ratio data, and in order to further evaluation of obtained results, the job's method of continuous variation was employed, between standard solutions of 10^{-3}M of metal ion with the ligand solution, 5.8×10^{-4} M.A series of solutions were prepared in which the total volume is 2 ml, with different mole ratios, (eg. 0-1). For evaluation of the formation constants of complexes K_f from the absorbance mole ratio data. The nonlinear least-squares curve-fitting program KINFIT was used [11-19].

Result and Discussion

For the cases of one step ML complex formation, the following equation could be derived using ligand concentrations equation for simple ML type [3].

$$M + L = ML \quad (1)$$

$$K_f = [ML] / [L][M] \quad (2)$$

$$CL = [L] + [ML] \quad (3)$$

$$CM = [Mn^{+}] + [ML] \quad (4)$$

Absorption spectra

In order to study of complex formation between Cu (II) with 2-[Phenyl – (Phenyl Hydrazino) – Methyl] Phenyl Amin, the absorption spectra of the ligand, Cu and ligand-Cu were investigated in the range of 200nm-400nm. Fig.1 illustrates a new spectrum that is due to formation of complex. The complexometric spectra for the complexation of Cu (II) with the ligand were represented in fig. 2. As it shown, the isosbestic point in 350nm and 380nm represents the complex formation.

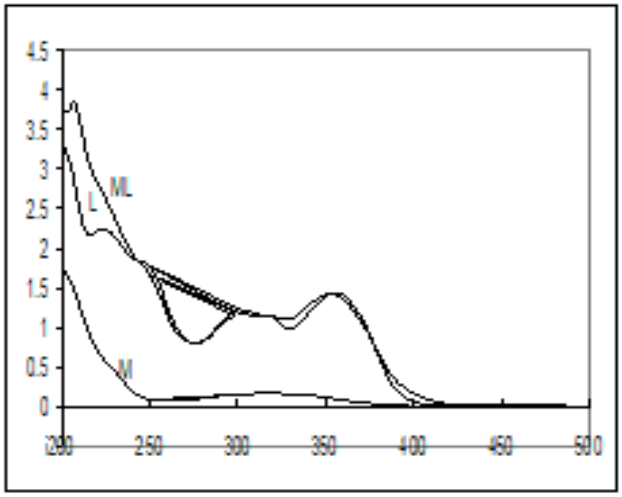

Figure 1: electronic UV-Vis absorption spectra of ligand (5.8×10^{-4}), Cu (10^{-3}M),) and ligand-Cu in acetonitrile

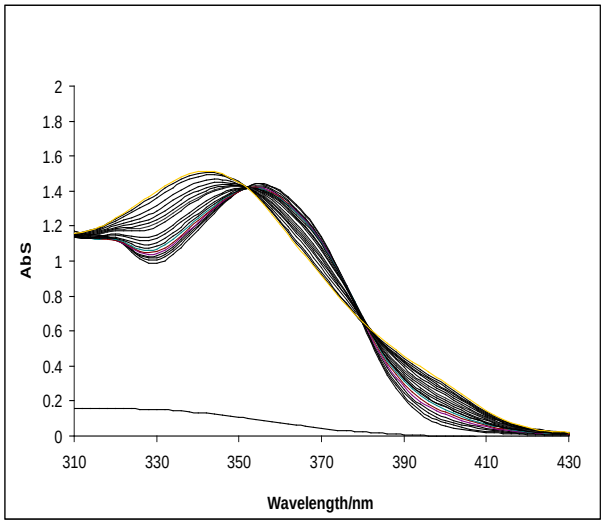

Figure 2: electronic UV-Vis absorption spectra of the ligand in the presence of Cu^{2+}. [Cu^{2+}] / [L].
Mole ratios are: 0.14, 0.28, 0.42, 0.56, 0.7, 0.87, 1, 1.12, 1.24, 1.36, 1.48, 1.16, 1.72, 1.84, 2, 2.12, 2.24, 2.36.

3.2 Mole ratio method

The stoichiometric ratio between Cu (II) ions and L in the complex was checked by the mole ratio method. The measured absorbance is plotted against the mole ratio $[Cu^{2+}]$ / [L] as show in fig.3 and the plot showed a certain break point confirmed that the molar ratio between Cu (II) and l in the complex is 1:1 and the complex is ML type.

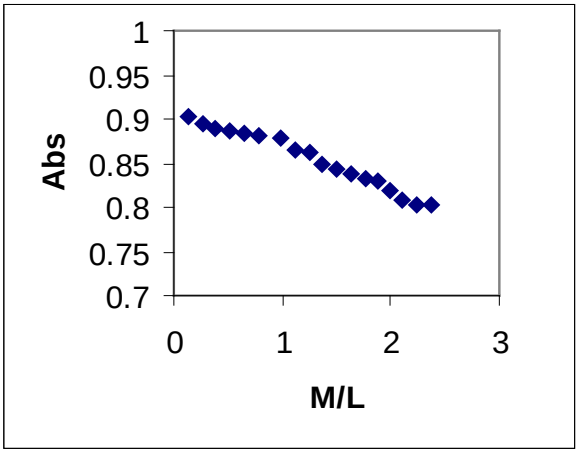

Figure 3: A plot of absorbance at 268nm as function of mole ratio of $[Cu^{2+}]$/ [L] in acetonitrile.

Kinfit program

Nowadays different programs such as the KINFIT and BEST programs have been used for evaluating the stability constant of complexes or dissociation constants of ligands, using spectrophotometric or potentiometric data [20]. The complex formation constant k_f were evaluated the absorbance-mole ratio data, the nonliner least-squares cure-fitting program KINFIT was used.

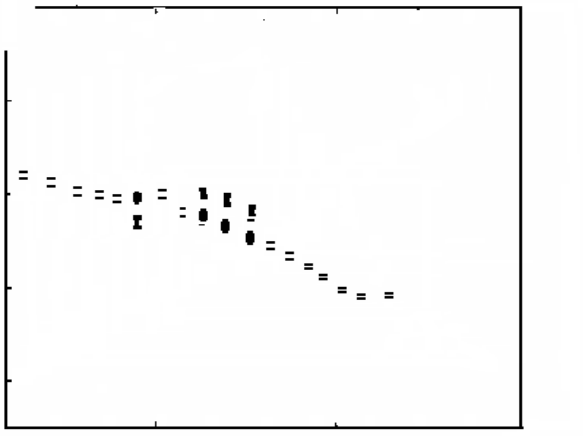

Figure 4: The corresponding Abs .Vs. $[Cu^{2+}]$/ [L] plot. Where is experimental point, 0 is estimated and = is matching point.

Job's method

To confirm the stoichiometry of complex, job's method was applied. Application of Job's method of continuous variation [21] indicated a 1:1 complexation ratio because of appearance of a peak in 0.5 mole ratio and spectrum of FT-NMR ligand and ligand-Cu illustrate in Fig 5a, 5b.

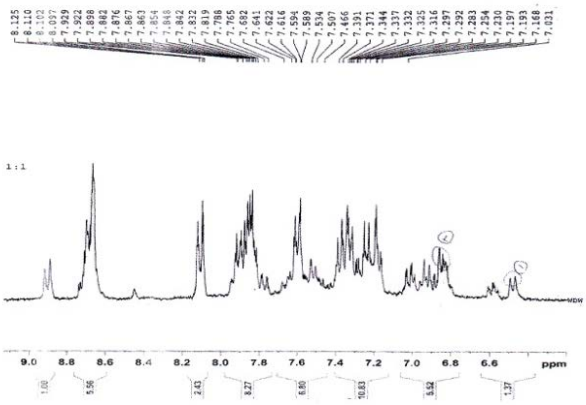

Figure 5a: Spectra of NMR for ligand – Cu

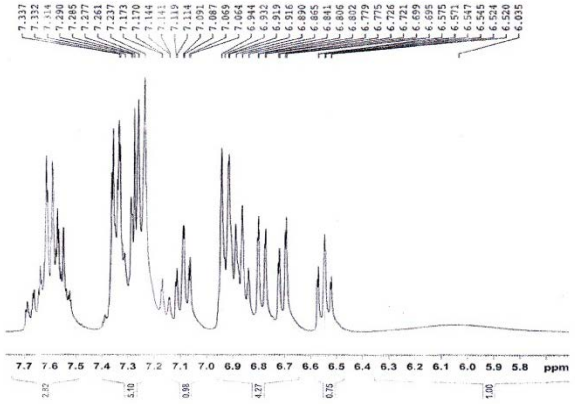

Figure 5b: Spectra of NMR for ligand

Result data are included in table 1.

Table 1. Resulting of IR spectrum of ligand-metal complexes in acetonitrile at 25°C. (S=Strong, b=broad).

Species	C-H Functional Group		N-H Functional Group		C=N Functional Group		C-N Functional Group	
	Wavenumber (cm^{-1})	Peak Description	Wavenumber (cm^{-1})	Peak Description	Wavenumber (cm^{-1})	Peak Description	Wavenumber (cm^{-1})	Peak Description
L	3054.2	s	3467.1	S	1600.49	s	1248.15	s
L-Cu^{2+}	3057.7	b	3441.89	b	1600.17	b	1250.71	b

In order to calculate the stability constants, the absorbance curve fitting program and mole ratio data was used by a non liner least square. The resulting data are shown in, table2.

Table 2: Formation constant values for ligand-mental complex in acetonitrile at 25°C.

Complex	L-Cu
Stoichiometry	Ml
K_f	2700

Conclusion

In this work, the synthesis and complexation reactions between 2-[Phenyl – (Phenyl Hydrazino) – Methyl]Phenyl amine and several transition metal ions include Cu^{2+} has been investigated in acetonitrile at room temperature using spectrophotometric methods. According to the recoded absorption spectra and observation of changes after each addition of cations in them, we can prove that complex formation was occurred. These changes include formation is isosbestic point, shift and intensity decrease of absorption spectra and appearance of new spectra that are related to the new formed complexes. Mole ratio plots showed a break point at the mole ratio of 1 that it means the complexes have ML stoichiometry. On the other hand the applied Job's method not only confirms the obtained results, but also determines the K_f value (formation constant).the formation of complexes was also confirmed by IR and NMR spectrometry. The K_f values were determinate using KINFIT program (computer fitting of absorbance-mole ratio data). According to the obtained K_f value for complexe, Cu^{2+} ion formed the strong.

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SHIMADZU 2550.
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REFERENCES:

1. Jackson K.W. and Chen G. (1996). Atomic Absorption Atomic Emission and Flame Emission spectrometry. Anal Chem, 68(12): 231-256.
2. Pekel N. and Guven O. (1999). Investigation of Complex Formation with Poly (N-vinyl imidazole) and Various Metal Ions Using the Molar Ratio Method. Colloid Polym Sci, 277(6): 570-573.
3. Venkatachalam L. (2004). The contingent valuation method. Envirn. Impact. Asses. Rev, 24(1): 89-124.
4. Gunasekaran N., Karvembu r., weng S. and Teikink. E.R.T. (2010). 1-Benzoil-33-Dibutilthiorea. Acata crystalloger. Sect E, 66(10): 2593- 2601.
5. Shamsipur M., Ershad s., Samadi N., Rezvani A.R. and Haddadzade H. (2005).Talanta, 65(4): 991-997.
6. Samadi N. and Ahari Salmasi M.J. (2013). Synthesis and Study of Complexation Reaction of a Newly Synthesized Ligand ((E-1-2-hydroxybenzylidene)-4-phenyl With Some Transition Metal Ions in Acetonitrile. Chem. Bio. Phy. Sci. Sec, A. 3(2): 1008-1016.
7. Sabzi R.E., Nokoo A., Nikzad Y., Bahram M., Akbari K. and Samadi N. (2012). Synthesis Determination of Stability Constants of a New Bis 1,2,4-triazole Ligand For Compleyation With Zinc, Copper and Nickel in Asetonitrile. Am J Anal, 3(6): 437-442.
8. Samadi N., Salamati M. and Nasseri A. (2013). Medel Based Multi-Warelength Spectrophotometric Method for Calculation of Formation Contants of Phenanthre-nequinone Thiosemicarbazone Complexes and Met-allic Cation. Current chemistry Letters, 2(2): 69-79.
9. Samadi N. and Ahari Salmasi M. (2013). Synthesis and Determination of Stability Constants of a New Coumarin Derivative with Some Transition Metal Ions in Acetonitrile. J. Biomed. Pharma. Res, 2(2): 16-20.
10. Ocak M., Gomrokoglu N., Ocak U., Buschman H.J. and Schollmeyer E. (2008). The Synthesis of New Triazole Ligands and Determination of Complex Stability Constants with Transition Metal Cations in Aqueous Media. J. Solution Chem, 37(11): 1489-1497.
11. Seleem H.S., El-Shetary B.A., Khalil S.M.E. and Sheble M. (2003). Potentiometric and Spectrophotometric Studies of the Complexation of Schiff-base Hydrazones Containing the Pyrimidine Moiety. J. Chem. Soc, 68(10): 729-731.
12. Safavi A. and Rastegarzadeh S. (1999). Cloud Point Extraction for the Determination of Copper in Environmental Samples by Flame Atomic Absorption Spectrometry. Anal. Sci, 15(2): 173-181.
13. Moghimi A., Shokrollahi A., Shamsipur M .and Aghabozorg H. (2004). X-ray Crystal Structure and Solution Studies of Hexacoordinated Mercury (II) Complex of a Pyridine Containing Proton Transfer Compound. J.Mol. Struct, 701(1): 49-56.
14. Moghimi A., Shokrollahi A., Shamsipur M., Aghabozorg H. and Shockravi A. (2003). Use of 1,3,5-triaminocyclohexane as a Compact Capping Ligand Permits Access to the Host-guest Chemistry of Chromium(III)-Nickel(II)-Cyanide Cage Clusters. Mass Spectrometry and Single Crystal X-ray Analysis

Confirm the Encapsulation of a Single Molecule of THF Within the Cluster Cavity. Inorg. Chem, 42(5): 1616-1624.

15. Patel R.N., Singh N., Shrivastava RP. Shukla K.K. and Singh P.K. (2002). Potentiometric and Spectrometric Study: Copper (II), Nickelv(II) and Zinc(II) Complexes with Potentially Tridentate and Monodentate Ligands. Proc. Indian Acad. Sci, 114(4): 115-124.

16. GaoH.W. and Zhao J.F. (2003). Stability Constants of Cobalt (II) and Copper (II) Complexes with 3-[(o-Carboxy-p-nitrobenzene)azo]Chromotropic Acid and Selective etermination of Copper(II) by Competition Coordination. Croat. Chem.Acta, 76(1): 1-6

17. Machado M., Cukrowski I., Gameiro P. and Soares H.M.V.M.(2003). Challenges in Modelling and Optimisation of Stability Constants in the Study of Metal Complexes With Monoprotonated Ligands:Part 1.A Glass Electrode Potentiometric and Polarographic Study of a Cu–TAPSO–OH System. Anal. Chim. Acta, 492(1): 105-119.

18. Bakr M.F. (2003).Thermodynamic Study of Complexation Phenomena of Some Alkaline Earth Metal (II) Complexes in Propanol-1-Water Mixtures at Various Temperatures. J.Chin.Chem. Soc, 50(3): 339-344.

19. Wang Y.M., Cheng T.H. and Liu G.C. (2000). Synthesis of Two Derivatives of 3,6,9-tri(carboxymethyl)-3,6,9 triazaundecanedioic Acid and the Stabilities of Their Complexes with Ca2+, Cu2+, Zn2+, Dy3+ and Gd3. J.Chin. Chem. Soc, 47(5):1083-1094.

20. Nicely V.A. and Dye L. A. (1971). General Purpose Curve Fitting Program for Class and Research Use. J. Chem. Educ, 48(7): 421-490.

21. Rose R. Advanced Ohysico-Chemical Experiments. Pitman. London. (1964).

