

## مطالعات ترمودینامیکی تشکیل کمپلکس یون‌های مس، جیوه، نیکل، روی، کادمیم و کبالت با لیگاندهایی از خانواده بی پیریدین‌ها از طریق هدایت‌سنجی و اسپکتروفوتومتری در حلال استونیتریل و مقایسه رفتار آن‌ها

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تاریخ دریافت: ۴ خرداد ۱۳۹۵ تاریخ پذیرش: ۳۰ مهر ۱۳۹۵

## Conductometric and Spectrophotometric Studies of the Thermodynamics Complexation of $\text{Cu}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Co}^{2+}$ Ions with (E)-(Pyridine-2-Ylmethylidene)({2-(E)-(Pyridine-2-Ylmethylidene)Amino]ethyl} Ligands in Acetonitrile Solution and Comparison of Their Behaviors

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Received: 24 May 2016

Accepted: 21 October 2016

### چکیده

یک لیگاند جدید از مشتقات بی پیریدین سنتز و مقادیر ثابت تشکیل کمپلکس با کاتیون‌های مس، نیکل، کادمیم، روی، جیوه و کبالت از طریق روش‌های هدایت‌سنجی و اسپکتروفوتومتری در دماهای مختلف در حلال استونیتریل تعیین شد. ثابت تشکیل کمپلکس‌ها در نسبت مولی ۱:۱ و ۱:۲ (یون فلزی به لیگاند) از فیت کامپیوتری داده‌های نسبت جذب مولی و داده‌های نسبت هدایت‌سنجی مولی در دماهای مختلف محاسبه گردید و مشخص شد که ترتیب کمپلکس‌ها در حلال استونیتریل به ترتیب مس < جیوه < روی < کبالت < کادمیم < نیکل < نقره می‌باشد. تغییرات آنتالپی و آنتروپی واکنش کمپلکس شدن از ثابت تشکیل وابسته به دما ارزیابی شد.

### واژه‌های کلیدی

اسپکتروفوتومتری؛ هدایت‌سنجی؛ ثابت تشکیل؛ لیگاند بی پیریدین.

### Abstract

A new pyridine derivative ligand, (E)-(Pyridine-2-ylmethylidene)({2-(E)-(Pyridine-2-ylmethylidene)amino]ethyl} has been synthesized and  $K_f$  value of its complexes with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Co}^{2+}$  has been determined by spectrophotometric and conductometric methods in acetonitrile at various temperatures. The formation constants ( $K_B = K_1 \times K_2$ ) of the 1:1 and 1:2 (metal ion to ligand) complexes were calculated by computer fitting of the absorbance-mole ratio data, and molar conductance-mole ratio data at different temperatures, and found that complexes to vary in acetonitrile solvent in the order of  $\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Ag}^+$ . The enthalpy and entropy changes of the complexation reaction were evaluated from the temperature dependence of formation constants.

### Keywords

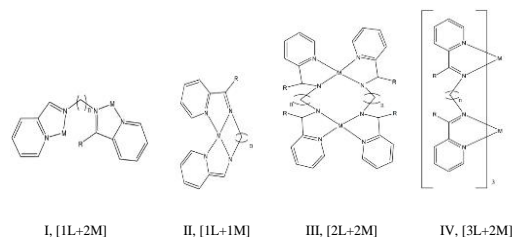
Spectrophotometry; Conductometry; Formation Constant; Pyridine Ligand.

### 1. INTRODUCTION

The coordination chemistry of pyridine, bipyridine (bipy), terpyridine (terpy), phenanthroline (phen), naphthyridine (naphthy) and pyridine-pyridazine (pyridaz) have received

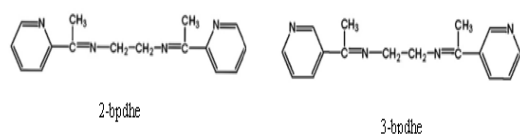
more and more attention since the late 19<sup>th</sup> century. Recent investigations on the unusual coordination features of these ligands were compared to classical chelating behavior to stimulate the synthesis of these complexes [1-3].

Schiff bases with bi- and tridentate pyridine-bis(imine) ligands have been the focus of research in polymer science for the polymerization of ethylene and propylene [4-5]. Coordination chemistry of these ligands with different metal to ligand ratios results in different geometries, such as tetrahedral [6], square planar, pentagonal bipyramidal [7], or octahedral [8-10] (Fig. 1, I-IV).



**Fig. 1.** General structure of the metal complexes with tetradentate di-Schiff bases (I-IV).

Organic ligands containing unsaturated nitrogen atoms can be regarded as soft Lewis bases. As such they may reveal high tendency to form stable coordination complexes with numerous transition metal ions, particularly those that can be regarded as soft Lewis acids [e.g., Cu (I) and Ag (I)][11]. Construction of transition metal complexes with specific network topologies (such as imines ligands) is one of the most interesting current research [12-13], because such complexes mimic zeolites [14-15] or other types of micro porous solids [16-17], and they afford functional materials with potentially controllable properties. These materials are used in molecular recognition and host-guest chemistry, catalytic applications, as well as optical, magnetic and electronic devices [18]. The poly - imines ligands were chosen as suitable building blocks to this end (Fig. 2). These compounds are flexible about the central C-C bond. Each of these ligands contains four potential sites for coordination to metal ions, the peripheral pyridyl-N as well as the inner imino N-atoms. In this work we focus on a series of new 2, 2' -bipyridyle - type organic ligands with added metal coordination functionality along the molecular backbone. The complexation process has been monitored by conductometry and UV/Vis absorption spectroscopy.



**Fig. 2.** Molecular structure of 2-bpdhe and 3-bpdhe ligands.

## 2. EXPERIMENTAL

### 2.1. Reagents

Reagent grade metals nitrates of copper, cobalt, zinc, nickel, cadmium and mercury (all from Merck) and recently imine ligands (2-bpdhe) and (3-bpdhe) synthesized were of highest purity available (>99%) and were used without any further purification.

Conductometric measurements were carried out by Metrohm 712 conductometer equipped with a Haake D1 circulator. In a typical experiment, 10.0 ml of metal ion solution ( $5.0 \times 10^{-5}$  mol L<sup>-1</sup>) in acetonitrile (AN) was placed in the two wall conductometer glass cell and the conductance of solution was measured. Then a known amount of the concentrated solution of imine type ligand in AN ( $5 \times 10^{-3}$  mol L<sup>-1</sup>) was added in a stepwise manner using a 10  $\mu$ l Hamilton syringe. The conductance of the solution was measured after each addition. The imine type ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

All UV-Vis Spectra recorded on a computerized double - beam Shimadzu 2550 spectrophotometer, using two matched 10.0 mm quartz cell. In a typical experiment, 2 .0 ml of ligand solution ( $5.0 \times 10^{-5}$  mol L<sup>-1</sup>) in acetonitrile was placed in the spectrophotometer cell and the absorbance of solution was measured. Then a known amount of the concentrated solution of metal ions in acetonitrile ( $1.3 \times 10^{-3}$  mol L<sup>-1</sup>) was added in a stepwise manner using a 10  $\mu$ l Hamilton syringe. The absorbance of the solution was measured after each addition. The metal ions solution was continually added until the desired ligand to metal ion mole ratio was achieved.

In order to have a better understanding of the thermodynamics of complexation between ligand and metal ions in acetonitrile, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the formation constants of the resulting complexes as a function of temperature with Vont Hoff Equation (1).

$$2.303 \log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

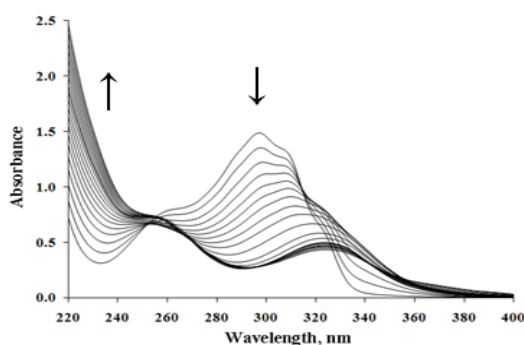
The formation constant ( $K_B = K_1 \times K_2$ ) and the molar absorptivity ( $\epsilon$ ) of the resulting 1:1 and 1:2 ( metal ion to ligand) complexes between the ligand and different metal ions at 25°C were calculated by fitting the observed absorbance,  $A_{obs}$ , at various metal ion/ligand mole ratios to the previously derived equations [19-20], which express the  $A_{obs}$  as a function of the free and complexed metal ions and the formation constant evaluated from a non linear least- squares program KINFIT [21].

For evaluation of the formation constant from molar conductance ( $\Lambda$ ) vs  $C_L/C_M$  mole ratio data, the KINFIT program was also used. Adjustable parameters are the  $K_f$ , molar conductance of free metal ion, and molar conductance of complex. The free metal ion concentration,  $[M]$  was calculated by a Newton - Raphson procedure. When the value of  $[M]$  had been obtained, the concentration of all other species involved are calculated from the mass balance equations by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum of squares of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standards deviation of the data [22].

### 3. RESULT AND DISCUSSION

#### 3.1. Spectrophotometric study

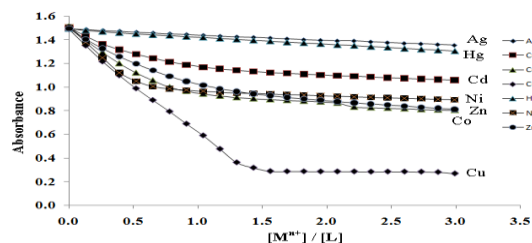
The electronic absorption spectrum of 3-bpdhe ligand its  $Cu^{2+}$  and complex in acetonitrile is shown in Fig. 3.



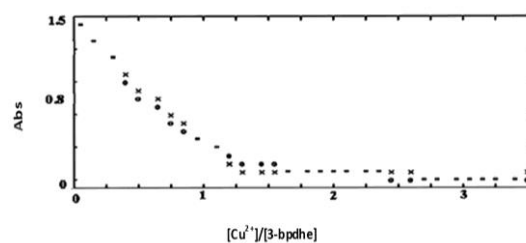
**Fig. 3.** The spectrum of ligand solution 3-bpdhe ( $5.0 \times 10^{-5} M$ ) in acetonitrile and increasing concentration of  $Cu^{2+}$  ion solution ( $1.30 \times 10^{-3} M$ ).

The stoichiometry of the metal complexes was examined by the mole ratio method at  $\lambda_{max}$  of its complexes. A sample of the resulting plots is shown in Fig. 4, 6 and it is evident that 1:1 and 1:2 (metal ion to ligand) complexes are formed in solution. The formation constants of the resulting complexes were obtained at 25°C by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts ( $5.0 \times 10^{-5}$  mol.  $L^{-1}$ ) of ligands solution, at  $\lambda_{max}$  of complexes. For evaluation of the formation constants and molar absorptivity coefficient from absorbance vs.  $[M]/[L]$  mole ratio data, a non - linear least squares curve fitting program KINFIT was used. A sample

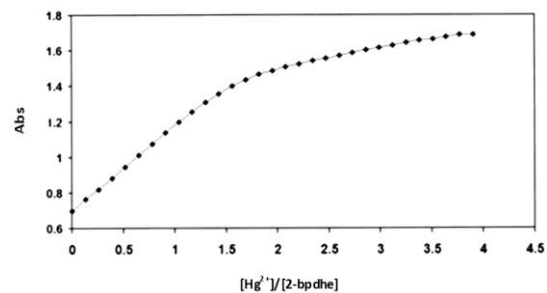
computer fit of the absorbance - mole ratio data for  $Cu^{2+}$  ion and 3-bpdhe at 25°C are shown in Fig. 5 and for  $Hg^{2+}$  ion with 2-bpdhe are shown in Fig.7 the resulting  $K_1$  of the 2-bpdhe and 3-bpdhe complexes at 25°C are listed in Table 1 and the resulting  $K_\beta$  at 25°C are listed in Table 2.



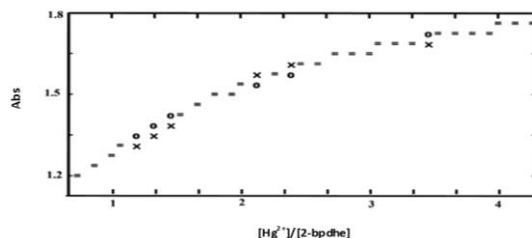
**Fig. 4.** Mole-ratio plots of absorbance as  $[M^{n+}]/[3-bpdhe]$  at 297.



**Fig. 5.** Computer fit of absorbance versus  $[Cu^{2+}]/[3-bpdhe]$  mole ratio plot in acetonitrile at 25°C, (x) experimental point, (o) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.



**Fig. 6.** Mole-ratio plot of absorbance as  $[Hg^{2+}]/[2-bpdhe]$  at  $\lambda_{max}$  of its.



**Fig.7.** Computer fit of absorbance vs.  $[Hg^{2+}]/[2-bpdhe]$  mole ratio in acetonitrile at 25° C, (x) experimental point, (o) calculated point, (=) experimental and calculated points are same within the resolution of the plot.

**Table 1.** Spectrophotometric formation constant for M (2-bpdhe) and M (3-bpdhe).

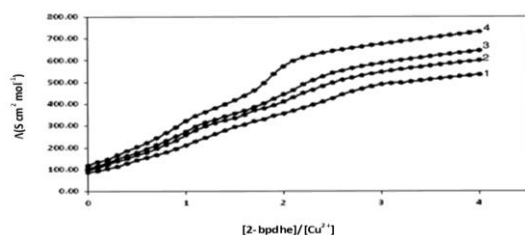
Complex	Cation	Log K <sub>1</sub>
M(2-bpdhe)	Hg <sup>2+</sup>	6.48±0.002
	Cu <sup>2+</sup>	3.62±0.002
	Zn <sup>2+</sup>	0.59±0.03
	Ni <sup>2+</sup>	0.57±0.02
	Cd <sup>2+</sup>	0.54±0.03
	Cu <sup>2+</sup>	5.24±0.02
M(3-bpdhe)	Ni <sup>2+</sup>	4.98±0.01
	Cd <sup>2+</sup>	4.75±0.01
	Zn <sup>2+</sup>	4.56±0.01
	Co <sup>2+</sup>	3.91±0.01
	Hg <sup>2+</sup>	2.95±0.02
	Ag <sup>+</sup>	1.44±0.02

**Table 2.** Spectrophotometric formation constant for M (3-bpdhe)<sub>2</sub>, M (2-bpdhe)<sub>2</sub>.

Complex	Cation	Log K <sub>β</sub> (Log K <sub>1</sub> +Log K <sub>2</sub> )
M(3-bpdhe) <sub>2</sub>	Hg <sup>2+</sup>	7.51±0.004
	Cu <sup>2+</sup>	7.38±0.001
	Zn <sup>2+</sup>	6.87±0.007
M(2-bpdhe) <sub>2</sub>	Hg <sup>2+</sup>	9.22±1.15
	Cu <sup>2+</sup>	6.9±0.003
	Zn <sup>2+</sup>	6.7±0.001
	Co <sup>2+</sup>	6.82±0.001

### 3.2. Conductometric studies

The molar conductance of the nitrate salts of Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> in acetonitrile solvent was monitored as a function of the imines ligand to metal ion mole ratio, and the stoichiometry of the complexes in acetonitrile was examined by the mole ratio method at variable temperatures. A sample of the resulting plots for Cu<sup>2+</sup> ion complex is shown in Fig. 8 and it is evident that ML and ML<sub>2</sub> complexes are formed in solution.

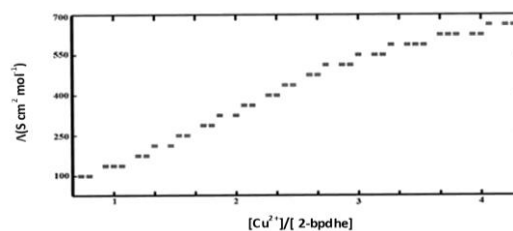
**Fig. 8.** Mole ratio plots of ligand 2-bpdhe with Cu<sup>2+</sup> ion complexes at various temperatures 5° C, 2) 15° C, 3) 25° C, 4) 35° C.

As it is seen while the ligand solution possesses a negligible conductance, its addition to all metal ion solutions in acetonitrile caused a rather large and continuous increased in molar conductance. This could be due to the lower mobility of the solvated cation and existence of some ion pairing in the initial salt. This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that transition metals ions strongly are complexed with acetonitrile and such a solvated ions will be highly ordered and sluggish (Marji et al., 1998).

The first additions of imines' ligand will complex with metals ions resulting in a more mobile system with relatively high conductivity. Further additions of ligand to the relatively mobile system will cause a gradual increase in conductivity. However, the slope of the corresponding molar conductance-mole ratio plots change at the point where the ligand to ions ratio are one, and further additions of the ligand cause no or very slight changes in the molar conductance. Such a conductance behavior is indicative of the formation of ML and ML<sub>2</sub> complexes in solutions.

The formation constants of the resulting complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand ( $5.0 \times 10^{-3}$  mol L<sup>-1</sup>) were added to fixed amounts ( $5.0 \times 10^{-5}$  mol L<sup>-1</sup>) of metals ions solution.

For evaluation of the formation constants from molar conductance vs. C<sub>L</sub>/C<sub>M</sub> mole ratio data, a non-linear least square curve fitting program KINFIT was used. A sample computer fit of the molar conductance-mole ratio data for Cu<sup>2+</sup> and 2-bpdhe at 25°C is shown in Fig.9.

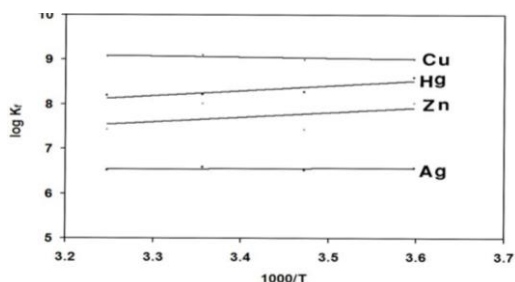
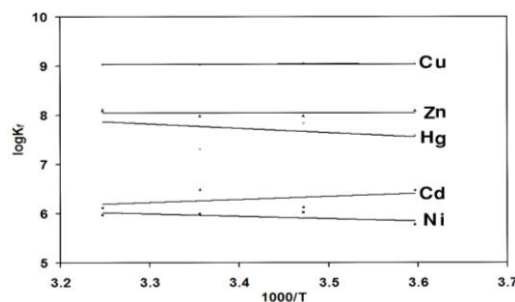
**Fig. 9.** Computer fit of molar conductance vs. [Cu<sup>2+</sup>] / [2-bpdhe] mol ratio plot in acetonitrile at 15° C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

All of log K<sub>β</sub> values evaluated from the computer fitting of the corresponding molar conductance-mole ratio data are listed in Table 3. Van't Hoff plots of log K<sub>β</sub> vs. 1/T, for Hg<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> complexes in acetonitrile were linear and are shown in Fig. 10,11. ΔH<sup>0</sup> and ΔS<sup>0</sup> values were determined from Van't Hoff Equation in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in Table 3.

Comprise of the data given in Table 3 indicate that the stability of the complexes to vary in the order Cu<sup>2+</sup> > Zn<sup>2+</sup> > Hg<sup>2+</sup> > Co<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> > Ag<sup>+</sup>. The thermodynamic data in Table 3 reveal that, enthalpy for formation of complexes for Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Co<sup>2+</sup> positive. It means that formation of these complexes is enthalpy desired and in all cases the complexes are entropy stabilized.

**Table 3.** Formation constants, enthalpies, and entropies for different M (3-bpdhe)<sub>2</sub> and M (2-bpdhe)<sub>2</sub> complexes in acetonitrile using conductometry.

Complex	Cation	Log K <sub>f</sub> ± SD				ΔH° (kJ mol <sup>-1</sup> )	ΔS° (Jmol <sup>-1</sup> K <sup>-1</sup> )
		5 °C	15 °C	25 °C	35 °C		
M(3-bpdhe) <sub>2</sub>	Cu <sup>2+</sup>	9.04±0.01	9.05±.001	9.03±0.002	9.03±0.002	0.8 ± 0.033	48.9 ±0.15
	Hg <sup>2+</sup>	7.59±0.01	7.84±0.004	7.31±0.006	8.13±0.006	17.3 ±1.5	89.79 ±5.10
	Cd <sup>2+</sup>	6.47±0.01	6.13±0.01	6.48±0.005	6.12±0.01	-11.48±0.85	35.3±2.9
	Ni <sup>2+</sup>	5.77±0.01	6.02±0.006	5.99±0.006	5.97±0.005	9.65±0.39	63.68±1.35
	Zn <sup>2+</sup>	8.1±0.01	7.99±0.006	7.99±0.008	8.9±0.11	15.85±1.48	87.62±5.05
M(2-bpdhe) <sub>2</sub>	Cu <sup>2+</sup>	9.02±0.01	9.01±0.003	9.10±0.003	9.08±0.003	4.40 ±0.128	81.8 ±0.437
	Hg <sup>2+</sup>	8.23±0.01	8.25±0.004	8.22±0.003	8.23 0.005	-21.02 ±0.4	38.04 ±1.4
	Ni <sup>2+</sup>	6.52±0.01	7.19±0.006	7.39±0.006	7.69±0.005	61.27±0.55	150.82±1.89
	Co <sup>2+</sup>	7.30±0.01	7.35±0.005	7.4±0.005	7.37±0.004	4.31±0.115	67.55±0.39
	Zn <sup>2+</sup>	8.03±0.01	7.44±0.02	8.015±0.01	7.44±0.009	-19.68±1.4	34.31±4.8
	Cd <sup>2+</sup>	6.81±0.01	7.05±0.009	6.77±0.007	6.78±0.002	-6.01±0.58	48.8±1.98
	Ag <sup>+</sup>	6.58±0.01	6.53±0.04	6.6±0.006	6.53±0.003	-22.36±0.16	52.61±0.55

**Fig. 10.** Log K<sub>f</sub> vs. 1/T for ion complexes with imine ligand 2-bpdhe.**Fig. 11.** Log K<sub>f</sub> vs. 1/T for ion complexes with imine ligand 3-bpdhe.

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