Iranian Journal of Analytical Chemistry
Volume 4, Issue 1, March 2017 (12-17)

مجله ایرانی شیمی تجزیه
دوره ۴، شماره ۱، فروردین ماه ۱۳۹۶ (۱۷-۱۲)

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

محمود پایه قدر[۱]، هما شفیع خانی[۱،*]، علی مرسلی[۲]
۱. بخش شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵، تهران، ایران
۲. دانشکده شیمی، دانشگاه تربیت مدرس، تهران، ایران

تاریخ دریافت: ٤ خرداد ۱۳۹۵ تاریخ پذیرش: ۳۰ مهر ۱۳۹۵

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

Mahmood Payehghadr[1], Homa Shafieekhani*[,1], Ali Morsali[2]
1. Department of Chemistry, Payame Noor University (PNU), P.O. BOX, 19395-3697, Tehran, Iran
2. Faculty of Chemistry, Tarbiat Modarres University, Tehran, Iran

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 اسپکتروفتومتری در دماهای مختلف در حلال استونیتریل تعیین شد. ثابت تشکیل کمپلکس‌ها در نسبت مولی ۱:۲و۱:۱(یون فلزی به لیگاند) از فیت کامپیوتری داده‌های نسبت جذب مولی و داده‌های نسبت هدایت سنجی 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 کمپلکس‌شدن از ثابت تشکیل وابسته به دما ارزیابی شد.

واژه‌های کلیدی

اسپکتروفتومتری؛ 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 Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and Co^{2+}has been determined by spectrophotometric and conductometric methods in acetonitrile at various temperatures. The formation constants ($K_ß = K_1 \times K_2$) 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 $Cu^{2+} > Hg^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+} > Ag^{+}$. The enthalpy and entropy changes of the complexation reaction were evaluated from the temperature dependence of formation constants.

Keywords

Spectrophotometry; Coductometry; Formation Constant; Pyridine Ligand.

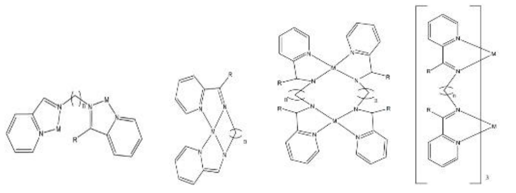
1. INTRODUCTION

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 19th 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].

---

*Corresponding Author: shafieehoma@yahoo.com

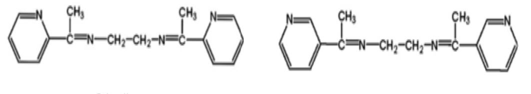
Schiff bases with bi- and tridentate pyridine-bis (imine) ligands have been the focus of research in polymer science for the polymerization of ethylene and propylene [4-5]. Coordination chemistry of these ligands with different metal to ligand ratios results in different geometries, such as tetrahedral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



I, [1L+2M] II, [1L+1M] III, [2L+2M] IV, [3L+2M]

Fig. 1. General structure of the metal complexes with tetra dentate 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.



2-bpdhe 3-bpdhe

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 (5.0×10^{-5} mol L^{-1}) 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 (5×10^{-3} mol L^{-1}) was added in a stepwise manner using a 10 µl 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 (5.0×10^{-5} mol L^{-1}) 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 (1.3×10^{-3} mol L^{-1}) was added in a stepwise manner using a 10 µl 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 Von't Hoff Equation (1).

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

The formation constant ($K_\beta = K_1 \times K_2$) and the molar absorptivity (ε) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between the ligand and different metal ions at 25ºC 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 (Λ) *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.

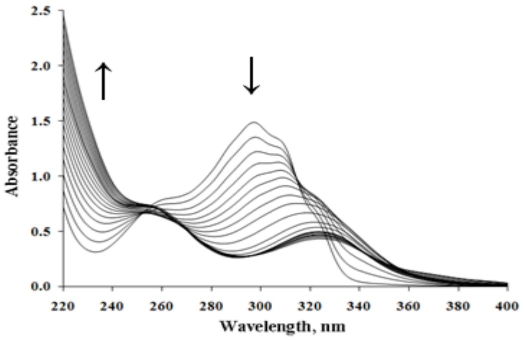


Fig. 3. The spectrum of ligand solution 3-bpdhe (5.0×10^{-5}M) in acetonitrile and increasing concentration of Cu^{2+} ion solution (1.30×10^{-3}M).

The stoichiometry of the metal complexes was examined by the mole ratio method at λ_{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 25ºC by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5.0×10^{-5} mol. L^{-1}) of ligands solution, at λ_{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_β at 25°C are listed in Table 2.

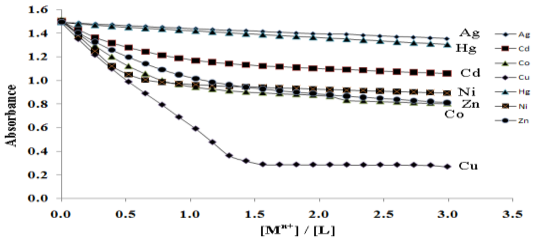


Fig. 4. Mole-ratio plots of absorbance as $[M^{n+}]/[3\text{-bpdhe}]$ at 297.

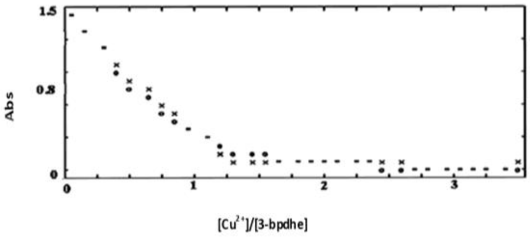


Fig. 5. Computer fit of absorbance versus $[Cu^{2+}]/[3\text{-bpdhe}]$ mole ratio plot in acetonitrile at 25ºC,(x) experimental point, (o) calculated point, (=) experimental and calculated points are the same withine the resolution of the plot.

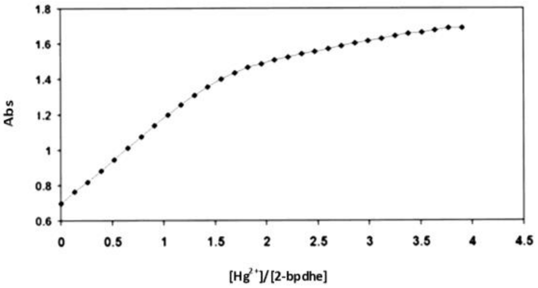


Fig. 6. Mole-ratio plot of absorbance as $[Hg^{2+}]/[2\text{-bpdhe}]$ at λ_{max} of its.

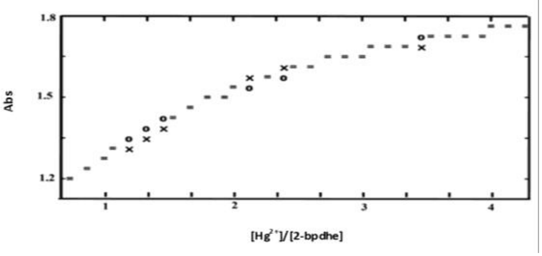


Fig.7. Computer fit of absorbance vs. $[Hg^{2+}]/[2\text{-bpdhe}]$ mole ratio in acetonitrile at 25º C, (×) experimental point, (o) calculated point, (=) experimental and calculated points are same within the resolution of the plot.

Table1. Spectrophotometric formation constant for M (2-bpdhe) and M (3-bpdhe).

Complex	Cation	Log K_1
M(2-bpdhe)	Hg^{2+}	6.48±0.002
	Cu^{2+}	3.62±0.002
	Zn^{2+}	0.59±0.03
	Ni^{2+}	0.57±0.02
	Cd^{2+}	0.54±0.03
M(3-bpdhe)	Cu^{2+}	5.24±0.02
	Ni^{2+}	4.98±0.01
	Cd^{2+}	4.75±0.01
	Zn^{2+}	4.56±0.01
	Co^{2+}	3.91±0.01
	Hg^{2+}	2.95±0.02
	Ag^{+}	1.44±0.02

Table 2. Spectrophotometric formation constant for M (3-bpdhe) $_2$,M (2-bpdhe) $_2$.

Complex	Cation	Log $K_β$(Log K_1+Log K_2)
M(3-bpdhe)$_2$	Hg^{2+}	7.51±0.004
	Cu^{2+}	7.38±0.001
	Zn^{2+}	6.87±0.007
M(2-bpdhe)$_2$	Hg^{2+}	9.22±1.15
	Cu^{2+}	6.9±0.003
	Zn^{2+}	6.7±0.001
	Co^{2+}	6.82±0.001

3.2. Conductometric studies

The molar conductance of the nitrate salts of Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+} 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^{2+}ion complex is shown in Fig. 8 and it is evident that ML and ML, ML_2 complexes are formed in solution.

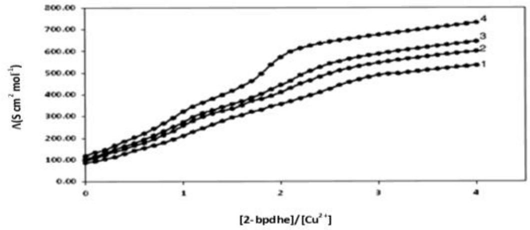


Fig. 8. Mole ratio plots of ligand 2-bpdhe with Cu^{2+} ion complexes at various temperatures 5° C, 2) 15° C, 3) 25 °C, 4) 35°C.

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_2 complexes in solutions.

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

For evaluation of the formation constants from molar conductance *vs.*C_L/C_M 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^{2+} and 2-bpdhe at 25°C is shown in Fig.9.

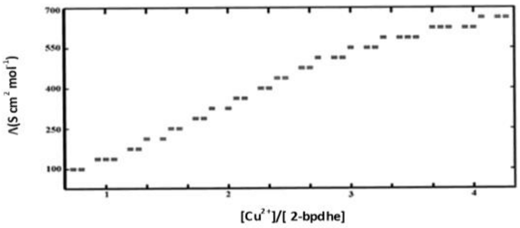


Fig. 9. Computer fit of molar conductance *vs.* [Cu^{2+}] / [2-bpdhe]mol ratio plot in acetonitrile at 15° C ,(X) experimental point,(O) calculated point ,(=) experimental and calculated points are the same within the resolution of the plot.

All of log $K_ß$ 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 $K_ß$ *vs.* 1/T, for Hg^{2+}, $Cu^{2+,}$ Ni^{2+}, Ag^{+}, Co^{2+} and Cd^{2+} complexes in acetonitrile were linear and are shows in Fig. 10,11. ΔH^0 and ΔS^0 values were determined from Van't Hoff Equation in the usual manner from the slops 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^{2+}> Zn^{2+} > Hg^{2+}> Co^{2+}> Cd^{2+} > Ni^{2+} > Ag^{+}. The thermodynamic data in Table 3 reveal that, enthalpy for formation of complexes for Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} 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)$_2$ and M (2-bpdhe)$_2$ complexes in acetonitrile using coductometry.

Complex	Cation	Log K_f± SD				ΔH° (kJ mol^{-1})	ΔS° (Jmo l^{-1} K^{-1})
		5 °C	15 °C	25 °C	35 °C		
M(3-bpdhe)$_2$	Cu^{2+}	9.04±0.01	9.05±.001	9.03±0.002	9.03±0.002	0.8 ± 0.033	48.9 ±0.15
	Hg^{2+}	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^{2+}	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^{2+}	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^{2+}	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)$_2$	Cu^{2+}	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^{2+}	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^{2+}	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^{2+}	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^{2+}	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^{2+}	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^{+}	6.58±0.01	6.53±0.04	6.6±0.006	6.53±0.003	-22.36±0.16	52.61±0.55

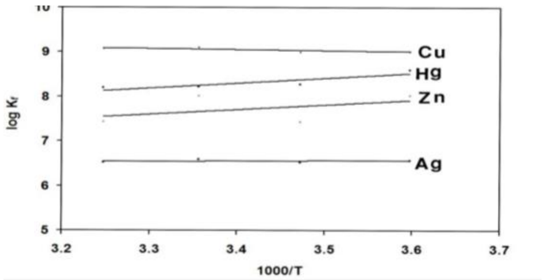


Fig. 10. Log K_f vs. .1/T for ion complexes with imine ligand 2-bpdhe.

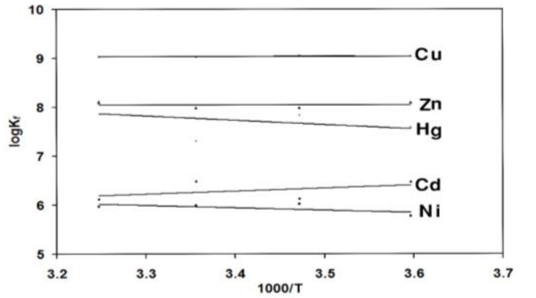


Fig. 11. Log Kf vs. .1/T for ion complexes with imine ligand 3-bpdhe.

REFERENCES

[1] R. Ziessel, Schiff-based bipyridine ligands. Unusual coordination features and mesomorphic behavior, *Coord. Chem. Rev.* 216-217 (2001) 195-223.

[2] P.A. Vigato and S. Tamburini, The challenge of cyclic and acyclic Schiff bases and related derivatives, *Coord. Chem. Rev.* 248 (2004) 1717-2128.

[3] C. Janiak, Engineering coordination polymers towards applications, *Chem. Soc. Dalton Trans.* 14 (2003) 2781-2804.

[4] S.D. Ittel, L.K. Johnson and M. Brookhart, Late-Metal Catalysts for Ethylene Homo- and Copolymerization, *Chem. Rev.* 100 (2000) 1169-1204.

[5] B.L. Small and M. Brookhart, Polymerization of Propylene by a New Generation of Iron Catalysts: Mechanisms of Chain Initiation, Propagation, and Termination, *Macromoleculares* 32 (1999) 2120-2130.

[6] C.M. Liu, R.G. Xiong, X.Z. You and Y.J. Liu, Crystal structure and some properties of a novel potent Cu_2Zn_2SOD model Schiff base copper (II) complex {[Cu (bppn)] $(ClO_4)_2$}$_2$·H_2O, *Polyhedron* 15 (1996) 4565-4571.

[7] J. Szklarzewicz, A. Samotus, J. Burgess, J. Fawcett and D.R. Russel, Structural and spectroscopic characterization of a dicyanooxomolybdenum(IV) complex with a tetradentate schiff-base ligand, *J. Chem. Soc. Dalton Trans.* 18 (1995) 3057-3061.

[8] S. Gourbatsis, S.P. Perlepes, I.S. Butler and N. Hadjiliadis, Zinc(II) complexes derived from the di-Schiff-base ligand *N,N′*-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine (L_A) and its hydrolytic-cleavage product *N*-[1-pyridin-2-yl)ethylidene]ethane-1,2-diamine(L): preparation, characterization and crystal structure of the 5-coordinate species [$ZnLCl_2$], *Polyhedron* 18 (1999) 2369-2375.

[9] P.K. Bowyer, K.A. Porter, A.D. Rae, A.C. Willis and S.B. Wild, From helicate to infinite coordination polymer: crystal and molecular structures of silver (I) complexes of readily prepared di-Schiff bases, *J. Chem. Soc. Chem. Commun.* 10 (1998) 1153-1154.

[10] S. Gourbatsis, N. Hadjiliadis, S.P. Perlepes, A. Garoufis and I.S. Butler, Structural and spectroscopic characterization of a cationic aquanitrato copper (II) complex with tetradentate Schiff- base ligand N, N'- bis[1-(2 - pyridyl) ethylidene] ethane – 1 , 2 - diamine, *Transition Met. Chem.* 23 (1998) 599-604.

[11] R.G. Pearson, The HSAB Principle - more quantitative aspects, *Inorg. Chim. Acta* 240 (1995) 93-98.

[12] P.J. Stang and B. Olenyuk, Self-Assembly, Symmetry, and Molecular Architecture: Coordination as the Motif in the Rational Design of Supramolecular Metallacyclic Polygons and Polyhedra, *Acc. Chem. Res.* 30 (1997) 502-518.

[13] D. Braga, Intermolecular Interactions in Nonorganic Crystal Engineering, *Acc. Chem. Res.* 33 (2000) 601-608.

[14] B.F. Abrahams, B.F. Hoskins, D.M. Michall and R. Robson, Assembly of porphyrin building blocks into network structures with large channels, *Nature* 369 (1994) 727.

[15] P. Schwarz, E. Siebel, R.D. Fischer, D.C. Apperley, N.A. Davies and R.K. Harris, Angew. $[(CoCp_2) \subset Fe\ (\mu\text{-}CNSnMe_3NC)_3]$: A Purely Organometallic Channel Inclusion Compound, *Chem., Int. Ed. Engl.* 34 (1995) 1197-1199.

[16] O.M. Yaghi, G. Li and H. Li, Selective binding and removal of guests in a micro porous metal–organic framework, *Nature* 378 (1995) 703.

[17] G.B. Gardner, Y.H. Kiang, S. Lee, A. Asgaonkar and D. Venkartraman, Exchange Properties of the Three-Dimensional Coordination Compound 1,3,5-Tris(4- ethynylbenzonitrile)benzene $\cdot AgO_3SCF_3$, *J. Am. Chem. Soc.* 118 (1996) 6946-6953.

[18] G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano and V. Balzani, Decanuclear homo- and heterometallic polypyridine complexes: syntheses, absorption spectra, luminescence, electrochemical oxidation, and inter-component energy transfer**,** *Perspect. Coord. Chem.* 114 (1992) 2944-2950.

[19] H. Khajesharifi and M. Shamsipur, Spectrophotometric study of the thermodynamics of complexation of lithium and sodium ions with dibenzo-24-crown-8 in binary dimethylsulfoxide-acetonitrile mixtures using murexide as a Metallochromic Indicator, *J. Coord. Chem* 35 (1995) 289-297.

[20] M. Payehghadr, A.A. Babaei, L. Saghatforoush and F. Ashrafi, Spectrophotometric and conductometric studies of the thermodynamics complexation of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions with a new schiff base ligand in acetonitrile solution, *Afr. J. Pure Appl. Chem.* 3 (2009) 092-097.

[21] M. Shamsipour, A. Avanes, G. Aghapour and H. Sharghi, Spectrophotometric studies of acidity constant and Cu^{2+} ion complexation of 1-Hydroxy-2-(prop-2’- enyl)-4-(prop-2’-enyl-oxy)-9,10-anthraquinone in methanol-water mixtures, *Pol. J. Chem.* 75 (2001) 1533-1541.