FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF BIVALENT Co, Ni, Cu AND Zn COMPLEXES WITH SCHIFF BASE LIGAND: EXPERIMENTAL AND DFT CALCULATIONS

Sheida Esmaielzadeh* and Ghazal Mashhadiagha

Department of Chemistry, Darab branch, Islamic Azad University, Darab, Iran

(Received November 18, 2016; revised May 20, 2017)

ABSTRACT. Formation constant ($K_f$) values of Schiff base ligand, $L = \text{methyl-2-}\{[1\text{-methyl-2-(aceton)ethylidynenitrilo}]\text{ethylamino-1-cyclopentenedithiocarboxylate}$, with Co(II), Ni(II), Cu(II) and Zn(II) ions has been determined spectrophotometrically for 1:1 complex formation at constant ionic strength 0.01 M (NaClO$_4$), and at various temperatures in DMF solvent. Thermodynamic studies of the complexes have been carried out and their stability were found in the order CoL $>$ CuL $>$ NiL $>$ ZnL. The enthalpy, entropy and Gibbs free energy changes of the complexation reaction have been evaluated from the temperature dependence of the formation constant. Our experimental results revealed that the complexation process is spontaneous, exothermic and entropically unfavorable. Also, B3LYP/(LANL2DZ and 6-311G**) level density functional theory is applied on the structure and stability of Schiff base ligand and their complexes. HOMO-LUMO and binding energies were calculated to obtained stability of the complexes. The theoretical results are compared with experimental data.

KEY WORDS: Metal complexes, Schiff base ligand, Formation constant, DFT calculation

INTRODUCTION

Stability constant can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as environmental studies, medicinal, analytical and industrial chemistry [1-4]. Therefore complexation reactions of metal ions with different ligands have been widely studied [5-7].

As an important class of compounds, Schiff bases have received much attention in the wide variety of fields due to structural varieties and unique characteristics such as preparative accessibility, varied coordination ability, thermal stability, biological activities and catalysis properties [8-10]. Schiff base ligands are able to coordinate with many different metals and stabilize them in various oxidation states [11-13].

A good deal of work has been reported on the preparation and structural investigation of Schiff base complexes. In addition Schiff base complexes possess a wide range of bioactivities and their chemistry, analytical, agricultural, industrial uses as catalyst and pharmacological applications have been extensively investigated [14-16].

In the search for the determination of stability constants for complexation process and the formation of Schiff base complexes several methods such as potentiometric titration [17], conductometric [18] and spectrophotometric determination [19], have been reported. Among the methods used for the determination of stability constants, spectrophotometric methods have the advantage of sensitivity and are suitable for determination of stability constants in solution under different experimental conditions.

In present work a Schiff base ligand methyl-2-{{1-methyl-2-(aceton)ethylidynenitrilo}-ethylamino-1-cyclopentenedithiocarboxylate, [H$_2$cdacMeen], synthesized [20] and the formation constant value ($K_f$) of its complexes with Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ has been determined spectrophotometrically. Also we report the thermodynamic parameter for the complexes.

*Corresponding author. E-mail: esmaielzadehsheida@yahoo.com
As a validation tool, our research group decided to compare the experimental data with the theoretical calculation. Previously the theory of transition metal chemistry has lagged behind the computational theory of organic chemistry because quantitative methods were more complicated. In recent years computational coordination chemistry is passing the infancy and gaining its momentum. The molecular mechanics and quantum mechanical theories are predicting comparative accurate results. A major place in the computational tools parameterization and substantiation is done by evaluating how well the experimental data are reproduced and comparing their correctness to the accuracy needed in the parameterization and substantiation of the particular method [21]. Thus in this paper in order to make sense between the experimental and theoretical results, formation constants of the titled Schiff base complexes were calculated by using DFT method. By increasing development of computational chemistry, DFT has been extensively used due to their accuracy and low computational cost to calculate a wide variety of molecular properties and provided reliable results which are in accordance with experimental [22-25].

**EXPERIMENTAL**

**Materials and apparatus**

The chemical used in this study were of analytical grade (cobalt acetate tetrahydrate, nickel acetate tetrahydrate, copper acetate tetrahydrate, zinc chloride monohydrate) from Merck. They were used as received. The unsymmetrical Schiff base ligand \([H_2cdacacMeen]\) was prepared according to reported method in our previous work [20]. All solution prepared fresh daily. The electronic absorption spectra in the UV-Vis region (250-700 nm) were obtained in DMF on Perkin Elmer double beam spectrophotometry using 1 cm path length quartz cells.

**Solution studies and complex formation measurements**

The formation constant measurements were carried out by a titration method at constant ionic strength 0.01 M (NaClO₄) at 15, 20, 25 and 30±1 °C. In duplicate experiments stock solutions of Schiff base ligand, \([H_2L]\), \((10^{-3} M)\) was prepared by dissolving an accurately weighed amount of the solid in DMF. The analytical ligand concentration was kept constant and different concentration of metal ions \((10^{-5}-10^{-4} M)\) in DMF were prepared and used as titrant. After preparation of the samples solution the time of one hour was given to the samples until they reach to the same as previous work [20, 25-27]. UV-Vis spectra were recorded in the range 250-700 nm. The SQUAD program [28] was used to calculate the formation constant of the resulting 1:1 complexes between \([H_2L]\) ligand and different metal ions. This program is designed to calculate the best values for the formation constants of the proposed equilibrium model by employing a non-linear least squares approach.

**Computational methods**

To investigate the stability of \([H_2L]\) Schiff base ligand and their complexes, in gas phase some properties such as HOMO-LUMO energies, chemical hardness and binding energy were obtained by using the gradient corrected density functional theory (DFT) method with the B3LYP functional [29] and LANL2DZ and 6-311G** basis sets. The Gaussian 03 package [30] was employed to perform geometrical optimization of all compounds used in this work.
RESULTS AND DISCUSSION

Thermodynamic interpretation

Unsymmetrical Schiff base complexes obtained from the reaction of the metal salts with the Schiff base donor ligand according to the following equation (1):

\[ [H_2L] + M(OAC)_2 \text{ or } M'Cl_2 \leftrightarrow [ML \text{ or } M'L] + 2\text{HOAC or } 2\text{HCl} \]  \hspace{1cm} (1)

\( M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, M' = \text{Zn}^{2+} \)

Interactions of metal salt with \([H_2L]\) were determined by UV-Vis absorption spectroscopy titration. The electronic spectra of the DMF solutions of the \([H_2L]\) free ligand, recorded in 250-700 nm exhibit bands at 314 nm and 398 nm assigned to the \(\pi\rightarrow\pi^*\) and \(n\rightarrow\pi^*\) transitions, respectively, of the azomethine and thiophen groups [31]. These bands are shifted to lower or longer wavelength in the complexes. The \(n\rightarrow\pi^*\) transition undergoes a blue shift, indicating that the lone pair electrons of oxygen and nitrogen are coordinated to the metal ion. The \(\pi\rightarrow\pi^*\) transition undergoes red shift with an increase in wavelength.

By addition of various concentrations of the metal salt to a solution of \([H_2L]\) ligand, the original band of \([H_2L]\) (\(\lambda_{max} = 314 \text{ and } 394 \text{ nm}\)) was weakened and a new weak band was appeared at (320-330 and 360-390 nm) for the formed product. This behavior suggests an instantaneous complex formation in solution from the reaction of the ligand under investigation with metal ion used. As an example Figure 1 show the created absorption spectra for a 1:1 metal-ligand complex formation system at 25 °C in DMF and at a constant ionic strength (0.01 M NaClO₄). The same changes are valid for other systems. The occurrence of isosbestic points during a reaction in very informative. Isosbestic points have been mentioned in the literature that presence of it means that the complex forms through equilibrium reactions [32]. Therefore, a clear isosbestic point at 301, 318, 373, 439 nm for this interaction (Figure 1) represents a reversible complex formation in solution.

![Figure 1](image_url)

Figure 1. The variation of the electronic spectra of \([H_2L]\) with Co(II) acetate at 25 °C in DMF.

In an attempt to explain why a given ligand prefers binding to one metal rather than another, it is necessary to the formation constant with the characteristic properties of metal ions. On the other hand, the thermodynamic parameters of metal ion Schiff base complex formation provide much significant information for studying these reactions and understanding the characteristic of corresponding complexes. The formation constant, $K_f$, of complexes were calculated at several temperatures using SQUAD computer program. This program is completely general in scope having the capability to refine formation constants for the general complex $M_m M_l H_j L_n L_q$, where $m, l, n, q \geq 0$ and $j$ are positive (for protons), negative (for hydrogen ion) or zero. The algorithm employed in SQUAD program [28].

Our input data for analysis of metal-ligand system were absorbance of 50 different wavelengths of $[H_2L]$ spectra, these spectra correspond to 15 various concentrations of metal solutions. The outputs are the logarithm of equilibrium formation constants, log $K_f$ for formation of $[ML]$. The results show that the best fitting corresponds to 1:1 complex model at all studied complexes. The formation constants data are collected in Table 1. Then the standard Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) changes of the formed complex were calculated. Van’t Hoff plots of these formation constant, lead to other thermodynamic parameters ($\Delta H$, $\Delta S$ and $\Delta G$).

The calculated thermodynamic parameters are listed in Table 1. On the basis of the results, the formation constant of the complexes with respect to bivalent transition metal ions were found in the order $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. In the studies systems, Schiff base ligand act as donor species and metal ion act as acceptor. $\text{Co}^{3+}$, $\text{Ni}^{2+}$ and $\text{Cu}^{+}$ with unoccupied d orbitals ($d^7$, $d^8$, $d^9$ system) have tendency to accept $\pi$-donation from Schiff base ligands, therefore Co complexes with lowest electron at d orbital have higher formation constant that other complexes. Our result revealed the formation constant for $\text{Cu}^{2+}$ are higher than $\text{Ni}^{2+}$ complexes which may be attributed to its positive charge distribution and the ligand deformation geometry. $\text{Cu}^{2+}$ with $d^9$ configuration tends to have a distorted square planar geometry because of John-Teller effect. $\text{Zn}^{2+}$ complex with fully occupied d orbitals ($d^{10}$ system) has low potency to accept electron from the Schiff base ligand and take a tetrahedral configuration, hence, it has the smallest formation constant [33]. On the other hand, this order ($\text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$) largely reflect the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion and the crystal field stabilization energies (CFSE) [34, 35].

Table 1. Thermodynamic parameters of the complexes in DMF.

<table>
<thead>
<tr>
<th>Complex</th>
<th>log $K_f$</th>
<th>$\Delta H^o$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^o$ (cal K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^o$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288</td>
<td>293</td>
<td>298</td>
<td>303</td>
</tr>
<tr>
<td>CoL</td>
<td>8.23(0.21)$^a$</td>
<td>7.96(0.13)</td>
<td>7.43(0.26)</td>
<td>7.02(0.11)</td>
</tr>
<tr>
<td>CuL</td>
<td>6.95(0.33)</td>
<td>6.08(0.03)</td>
<td>5.83(0.09)</td>
<td>5.26(0.07)</td>
</tr>
<tr>
<td>NiL</td>
<td>4.83(0.14)</td>
<td>4.25(0.25)</td>
<td>3.88(0.08)</td>
<td>3.21(0.28)</td>
</tr>
<tr>
<td>ZnL</td>
<td>4.06(0.24)$^a$</td>
<td>3.69(0.16)</td>
<td>3.12(0.51)</td>
<td>2.94(0.16)</td>
</tr>
</tbody>
</table>

$^a$Standard deviations are given in parentheses. $^a$at T = 303 K.
The data in Table 1 reveals that all the metal complexes are accompanied by negative enthalpy changes (ΔH) suggesting that the metal-ligand bonds are fairly strong. The entropy values of all complexes are negative. The combination of metal ions with Schiff base ligand decreased the degree of freedom of the system and entropy was decreased [36]. Negative values for (ΔG) show that these complex formations are energetically favorable and that the reaction proceeds spontaneously.

Figure 2. Perspective view of Schiff base ligand and their complexes (a) [H₂L] ligand, (b) [CoL], (c) [NiL], (d) [CuL] and (e) [ZnL], with atom labeling scheme.
DFT optimized structures

B3LYP/6-311G** optimized geometries of \([H_2L]\) (Figure 2) shows the mentioned ligand can act as an NNOS tetradentate chelating agent using the thiol sulfur atom (4S), the nitrogen atom (2N) from (N=CCH\(_3\)) group, the primary nitrogen atom (3N) and the hydroxyl oxygen atom (5O). The title ligand contains two planar fragments, viz. the cyclopentene and ketone moieties. As is usually observed in free s-alkyldithiocarbazates, the thiol sulfur atom in \([H_2L]\) is on the same side as the N=CCH\(_3\) group nitrogen atom. In the Table 2 provides selected structural information.

The ligand uses its four atoms to link the metal ion. Therefore, the metal centre is in a tetracoordinated environment and the geometry about the metal ions could be described as square planar for [NiL], square planar distorted for [CuL], tetrahedral distortion of the square planar for [CoL] and tetrahedral geometry for [ZnL] complexes. The optimized structure of all complexes with labeling of atoms is shown in Figure 2.

Table 2. The significant bond lengths (Å) and bond angles (°) of optimized metal Schiff base complexes, labels for atoms can be found in Figure 2.

<table>
<thead>
<tr>
<th>Bond</th>
<th>CoL</th>
<th>NiL</th>
<th>CuL</th>
<th>ZnL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3N-8C</td>
<td>1.33</td>
<td>1.33</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>2N-1C</td>
<td>1.34</td>
<td>1.34</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>M-3N</td>
<td>1.95</td>
<td>1.90</td>
<td>1.97</td>
<td>2.07</td>
</tr>
<tr>
<td>M-2N</td>
<td>1.95</td>
<td>1.90</td>
<td>1.97</td>
<td>2.06</td>
</tr>
<tr>
<td>M-4S</td>
<td>2.28</td>
<td>1.90</td>
<td>2.16</td>
<td>2.43</td>
</tr>
<tr>
<td>M-5O</td>
<td>1.88</td>
<td>1.91</td>
<td>1.94</td>
<td>1.98</td>
</tr>
<tr>
<td>Bond angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5O-M-2N</td>
<td>92.7</td>
<td>90.6</td>
<td>95.3</td>
<td>90.4</td>
</tr>
<tr>
<td>4S-M-3N</td>
<td>92.6</td>
<td>90.6</td>
<td>98.1</td>
<td>95.3</td>
</tr>
<tr>
<td>3N-M-2N</td>
<td>110</td>
<td>90.5</td>
<td>85.7</td>
<td>108</td>
</tr>
<tr>
<td>4S-M-5O</td>
<td>144</td>
<td>90.5</td>
<td>87.0</td>
<td>145</td>
</tr>
<tr>
<td>2N-1C-17C-18C</td>
<td>2.80</td>
<td>3.52</td>
<td>1.96</td>
<td>6.33</td>
</tr>
<tr>
<td>5O-18C-17C-1C</td>
<td>0.299</td>
<td>0.080</td>
<td>0.632</td>
<td>4.41</td>
</tr>
<tr>
<td>3N-8C-12C-13C</td>
<td>4.72</td>
<td>6.35</td>
<td>3.31</td>
<td>8.46</td>
</tr>
<tr>
<td>4S-13C-12C-8C</td>
<td>1.25</td>
<td>0.551</td>
<td>3.14</td>
<td>5.70</td>
</tr>
<tr>
<td>3N-M-3O-18C</td>
<td>93.0</td>
<td>106</td>
<td>83.2</td>
<td>93.8</td>
</tr>
<tr>
<td>2N-4S-13C</td>
<td>110</td>
<td>123</td>
<td>97.8</td>
<td>101</td>
</tr>
<tr>
<td>4S-2N-1C</td>
<td>66.0</td>
<td>50.2</td>
<td>80.1</td>
<td>106</td>
</tr>
<tr>
<td>8C-3N-M-5O</td>
<td>97.4</td>
<td>81.7</td>
<td>110</td>
<td>114</td>
</tr>
<tr>
<td>18C-5O-M-3N</td>
<td>93.0</td>
<td>106</td>
<td>83.2</td>
<td>93.8</td>
</tr>
</tbody>
</table>

The [NiL] complex adopts a nearly perfect square planar geometry: (i) the bond lengths associated with the nickel atom are virtually equal (Table 2), (ii) the two diagonal angles 3N-Ni-5O and 2N-Ni-4S of 179 and 179, respectively, barely deviate from linearity, (iii) the sum of the angles at nickel is very close to 360°, and (iv) as a result, the metal centre is located 0.003Å from the mean NNOS plane. Such a behavior is similar to those observed in related Ni(II) unsymmetrical Schiff base complex reported by us [26].

As implied by the selected bond lengths and bond angles (Table 2) the [CuL] complex, does not have ideal square planar geometry. Bond lengths to the 2N-Cu, 3N-Cu is similar at 1.97, 1.97 Å, respectively. The Cu-N distances are longer than that of Cu-O (1.94 Å). There is a slight distortion in the square planar geometry of copper. The angles 2N-Cu-3N, 3N-Cu-4S, 2N-Cu-5O and 4S-Cu-5O deviation substantially from that expected for an ideal square planar structure.
The dihedral angles between the two planes (3N-Cu-4S and 2N-Cu-5O) are 7.5° compared to 0° for a perfectly square planar arrangement and 90° for a perfect tetrahedral arrangement.

In [CoL] complex, the dihedral angle θ between the two 2N-Co-3N and 4S-Co-5O terminal planes is 75.7 (20)° and 75.2 (20)°. This shows deviations from tetrahedral to square planar. The wide range of angles observed around the metal centers (from 92.7 to 144) also shows the deviation from the ideal tetrahedral geometry. The Co-N bond distance (1.95 and 1.95 Å), is similar to that found in other complexes containing similar ligands [37]. The complex has a distorted tetrahedral coordination around the metal ion. The correct stereochemistry was assured through, manipulation and modification of the molecular coordinates to obtain reasonable and low energy molecular geometries. Energy minimization was repeated several times to find the minimum. The change in bond length values of metal-nitrogen and metal-oxygen in the complexes compared with ligand further suggest their coordination. The details of the bond lengths and bond angles of the metal complexes optimized by B3LYP/(LANL2DZ and 6-311G**) calculations are given in Table 2.

**HOMO and LUMO analysis**

The HOMO and LUMO orbitals are main orbital take part in chemical stability. The [H₂L] Schiff base ligand and their complexes HOMO/LUMO orbital pictures are depicted in Figure 3. The LUMO surface in the ligand, mostly is delocalized on the cyclopentene ring and sulfur atoms. In the surface shown for the HOMO level, the C=N group is overlapped. The LUMO surface of the complex mostly delocalized within the non-metallic atoms and for the HOMO level the metal atom is overlapped. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. LUMO can be thought the inner most orbital containing free places to accept electrons. Owing to the interaction between HOMO and LUMO orbitals, transition of π→π* type was observed with regard to molecular orbital theory. The energy difference between HOMO and LUMO orbitals, so called as energy gap, is an important stability for structures. The HOMO-LUMO energy gap of the ligand and the complexes calculated at B3LYP/(LANL2DZ and 6-311G**) level are shown in Table 3. A large HOMO-LUMO energy gap increase stability and decrease chemical reactivity [38, 39]. The calculation results confirm that the cobalt complex [CoL] is the most stable than other complexes and the stability of complexes decreases in the sequence: [CoL] > [CuL] > [NiL] > [ZnL]. This is good agreement to the studies of complex formation in experimental section.

Table 3. HOMO, LUMO, band gap and interaction energies of the complexesB3LYP/(LANL2DZ and 6-311G**).

<table>
<thead>
<tr>
<th>Complex</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Δ Band gap (eV)</th>
<th>Hardness (µ)</th>
<th>ΔE (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoL</td>
<td>-0.195</td>
<td>-0.0512</td>
<td>0.144</td>
<td>0.07199</td>
<td>-986</td>
</tr>
<tr>
<td>CuL</td>
<td>-0.192</td>
<td>-0.0489</td>
<td>0.143</td>
<td>0.07142</td>
<td>-959</td>
</tr>
<tr>
<td>NiL</td>
<td>-0.187</td>
<td>-0.0460</td>
<td>0.141</td>
<td>0.07040</td>
<td>-935</td>
</tr>
<tr>
<td>ZnL</td>
<td>-0.182</td>
<td>-0.0479</td>
<td>0.134</td>
<td>0.06703</td>
<td>-855</td>
</tr>
</tbody>
</table>

The hardness corresponds to the gap between HOMO and LUMO orbital. Absolute hardness is half of the HOMO-LUMO gap. Hence, the larger HOMO-LUMO energy gaps the harder molecule.

\[
\eta = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) \tag{4}
\]

According to the maximum hardness principle, greater hardness ($\eta$) causes more stability in the molecule [40]. As seen from Table 3 [CoL] complex have a higher hardness and is stable than the other complexes.

(a)  

(b)  

(c)
Figure 3. Plot of HOMO (left) and LUMO (right) calculated molecular orbital levels for the ligand Schiff base and their complexes (a) [H₂L] ligand, (b) [CoL], (c) [NiL], (d) [CuL] and (e) [ZnL], computed at B3LYP/(LANL2DZ and 6-311G**).

**Interaction energy**

In present research, the binding energy (ΔE) of complexes were calculated by B3LYP/(LANL2DZ and 6-311G**) level to predict the interaction between the Schiff base and various metal ions. The ΔE calculated as the difference between the energy complex with the optimized geometry (E_{complex}) and the sum of energies of the optimized ligands (E_{ligand}) and fragments [M(OAC)_2] where M = Co, Ni, Cu and ZnCl₂ was used to analyze their stability (Table 3). Their binding energy was calculated using equation 4:

\[ \Delta E = [E_{complex}] - [E_{ligand} + E_{metal ion}] \]  

(5)

These calculation results reveal that the cations with more negative binding energies are more susceptible for reaction with the ligand. These theoretical results are in accordance with our observations formation constant in the experimental method.

Although the present DFT calculations do not predict the exact trend observed in the extraction power of the Schiff base ligand, but they enable us to say which cations are more susceptible for extraction by the ligand or may act as interferences.
CONCLUSION

The present study allowed us to obtain the formation constant of Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes. The formation constant, $K_f$, of complexes were calculated at several temperatures using SQUAD computer program. Then the thermodynamic parameters such as standard Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) changes of the formed complex were calculated. The trend of the complex formation of the Schiff base ligand ($H_2cdacacMeen$) with four transition metal ions decreases as follow: [CoL] > [CuL] > [NiL] > [ZnL]. The molecular properties of the structures such as hardness, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, interaction energy, bond lengths and bond angles have been investigated by means of computational studies. These calculations have shown that the trend in HOMO-LUMO gap for the complexes follows: [CoL] > [CuL] > [NiL] > [ZnL]. This finding is further supported by the fact that the experimental formation constants of these complexes.

ACKNOWLEDGEMENT

We are grateful to Islamic Azad University, Darab branch Council for their financial support.

REFERENCES

7. Iravani, S.; Rou Naghi, G.; Ebrahim, M. Thermodynamic study of complexation reaction between 1,7,10,16 tetraoxa-4,13-diaza cyclooctadecane(kryptofix22) and Ni$^{2+}$, Cd$^{2+}$ and Ag$^{+}$ metal cations in some pure and binary mixed non-aqueous solvents using conductometry. Russ. J. Electrochem. 2016, 52, 1015-1020.


