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Spectrophotometric Study of Complexation of Dibenzopyridino–18-Crown–6 with Some Transition and Post-Transition Metal Ions in DMSO Solution Using Murexide as a Metallochromic Ligand[1]

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Abstract—The complexation reaction of dibenzopyridino-18-crown-6 (DBPY18C6) with Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, and Ag^+ have been studied in DMSO at 25°C by the spectrophotometric method. Murexide was used as a competitive colored ligand. The stoichiometry of metal ion-murexide and metal ions with DBPY18C6 complexes were estimated by mole ratio and continuous variation methods and emphasized by the KINFIT program. The stoichiometry of all the complexes was found to be 1 : 1 (metal ion/ligand). The order of stability constants for the obtained metal ion–murexide complexes (1 : 1) varies in the order $Cu^{2+} > Cd^{2+} > Co^{2+} \sim Pb^{2+} > Zn^{2+} > Ag^+ > Hg^{2+}$. This trend shows that the transition metal ions clearly obey the Irving–Williams role. For the post-transition metal ions, the ionic radius and soft-hard behavior was the major affects in varying of this order. The dibenzopyridino-18-crown-6 complexes with the used metal ions vary as $Ag^+ > Pb^{2+} > Cu^{2+} > Cd^{2+} > Hg^{2+} > Zn^{2+} > Co^{2+}$.

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INTRODUCTION

Throughout the synthesis of crown ethers, the selectivity behaviors of these compounds were recognized by Pedersen [1, 2]. The primary crown ethers contain only oxygen binding sites, which have tendency for selective binding with alkali and alkaline-earth metal ions [3, 4]. The selectivity is the prime request for most chemical measurements, especially, in analytical techniques [5]. The synthesis of new crown ethers, which have more tendencies for binding with transition and post-transition metal ions, was the more stimulated goal for research [6]. Therefore, new macrocyclic polyethers, which introduced N, S, and pyridyl unit onto macrocyclic ring, have been synthesized later [7, 8]. One of these new synthesized crown ethers is dibenzopyridino–18-crown–6 (**DBPY18C6**). Currently, our research group have studied the chemical behavior of DBPY18C6 in several areas, such as charge-transfer reactions with iodine [9], designing of ion-selective electrode and ion-transport for Pb^{2+} [10, 11], and potentiometric study of it with both some alkaline and alkaline-earth and post-transition metal ions in methanol [12–14]. We also studied the chemical behavior of DBPY18C6 with some alkaline-earth and lanthanides metal ions by spectrophotometry [15, 16]. In continuing these studies for approaching the analytical aspects, we have interested in studying complexation reactions of DBPY18C6 with some transition and post-transition metal ions by spectrophotometry, because there is no report about them in the literature [17, 18].

In spectrophotometric method, metal ion indicators have a considerable potential for obtaining reliable complex stability constants. The concentration of both the free ligand and the complex can be accurately measured without disturbing the equilibrium [19]. An important application of this approach is the measurement of stability constants of a metal ion with other ligands in solution. A competitive spectrophotometric method for the complexation studies of some transition and post-transition metal ions with crown ethers and cryptands have been developed [20–24], using murexide (**Mu**) as a suitable metallochromic indicator [23]. However, reports about murexide reaction with post-transition metal ion are quiet sparse [19, 25, 26]. Because of biological, industrial, and environmental importance of Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, and Hg^{2+} the study of the complexation, reactions of these metal ions with DBPY18C6 by the spectrophtometric method through using murexide was the major goal of this research.

In this study, we have reported the stability constants of complexation reactions of dibenzopyridino–18-crown–6 with Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, and

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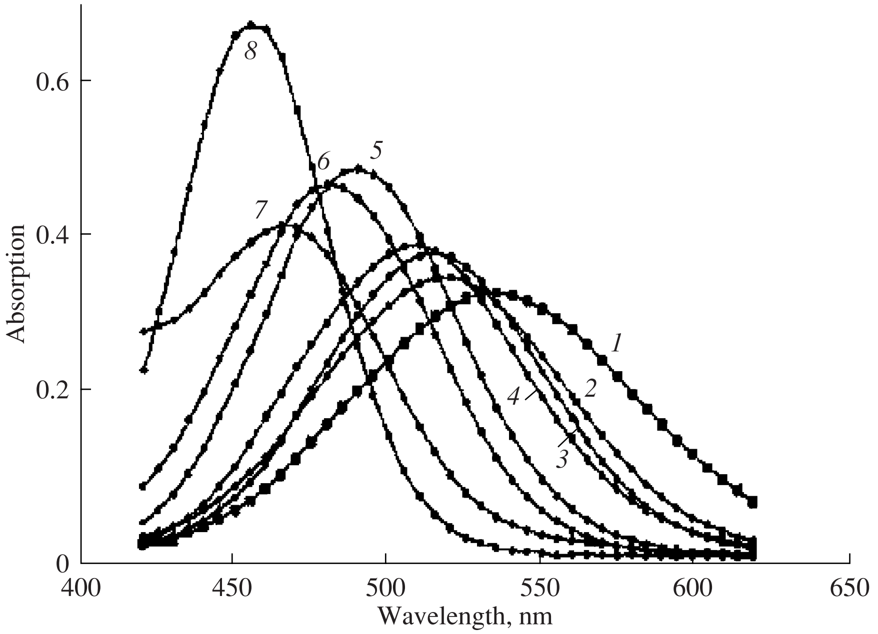
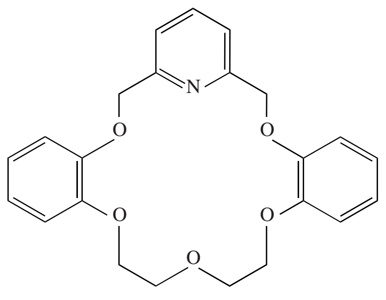
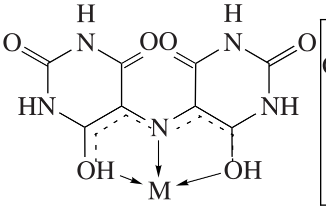


Fig. 1. Absorption spectra of 4.0×10^{-5} M murexide (*1*), and its complex with 4.0×10^{-3} M solutions of Ag^+ (*2*), Pb^{2+} (*3*), Hg^{2+} (*4*), Cu^{2+} (*5*), Cd^{2+} (*6*), Co^{2+} (*7*), and Zn^{2+} (*8*) in DMSO solution at 25°C.

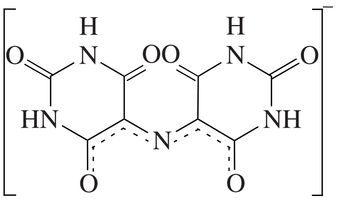
Hg^{2+} in DMSO, and also stability constants of complexes of murexide with metal ions (**I**):



DBPY18C6



(**I**)



(Murexide)

EXPERIMENTAL

Materials and method. Reagent grade nitrate salts of cobalt, copper, zinc, cadmium, silver, lead, and mercury chlorides and murexide of the highest purity were available and used without further purification, except for vacuum drying over P_2O_5. DBPY18C6 and reagent grade DMSO were also used as received (all from Merck).

All spectra were recorded on a Cecil 3000 spectrophotometer, which was connected to a personal computer. In a typical experimental run, 2 ml of murexide (4.0×10^{-5} M) in DMSO was placed in the spectrophotometer cell and thermostated at 25°C. Then a known amount of a metal solution (5–10 μl of 4.0×10^{-3} M) was added in a stepwise manner by using a calibrated microsyringe. The spectra of the solution after attainment of equilibrium were recorded. Addition of the metal ion solution was continued until the metal ion to murexide mole ratio was clearly achieved. The same procedure has been performed in the presence of DBPY18C6. Hence, 2 ml of a murexide solution (4.0×10^{-5} M) as colored ligand and 240 μl of DBPY18C6 (1.0×10^{-2} M) with ratio [DBPY18C6] : [murexide] = 30 were titrated with a concentrated metal ion solution (4.0×10^{-3} M).

RESULTS AND DISCUSSION

The ammonium salt of purpuric acid, 5-[hexahydroxy–2,4,6-trioxo-5-pyrimidinyl)imino]–2,4,6-(1H,3H,5H)pyrimidinetrione, monoamonium salt of murexide, is a tridentate chelating ligand, which has been used for many years as a suitable complexing agent for a large number of metal ions over a wide range of experimental conditions. The absorption spectra of 4.0×10^{-5} M murexide and its complexes with Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, and Hg^{2+} in DMSO solution were recorded and shown in Fig. 1. The lithium salt of murexide is 5-coordinated in a square pyramidal conformation with the base formed by the three donor atoms O, N, and O from one anion and carbonyl

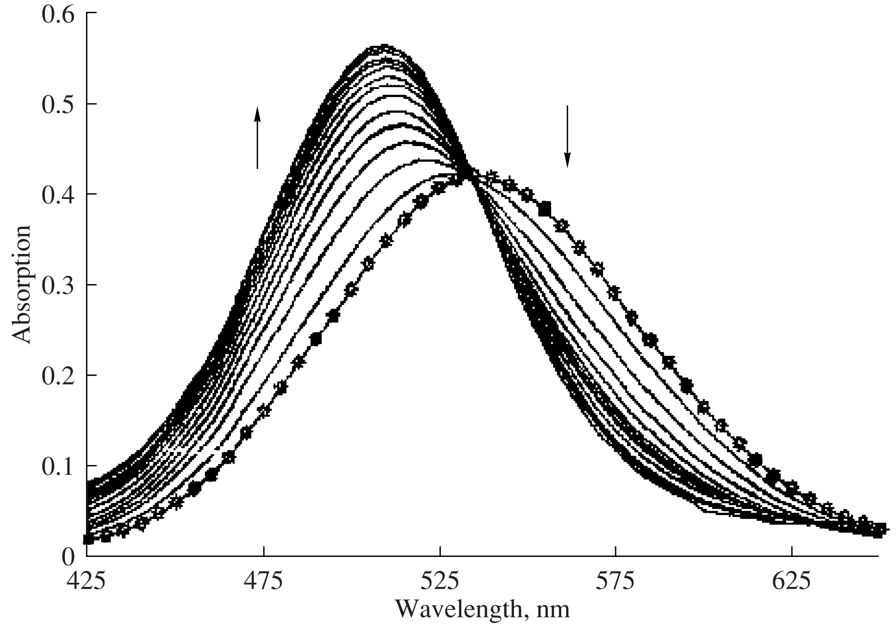


Fig. 2. Absorption spectra of 4.0×10^{-5} M murexide with Hg^{2+} ion (4.0×10^{-3} M) in the presence of DBPY18C6 (1×10^{-2} M) in DMSO at 25°C. Respective Hg^{2+}/murexide mole ratios in different solutions: 0.1, 0.25, 0.5, 1, 1.25, 1.5, 1.75, 2, 2.5, 3, 3.5, and 4.

oxygen from another [27]. So, the suggested structure for complex formation of murexide with metal ion is the structure **I**. Therefore, the spectral behavior of the complexes is quite unique in all cases, consisting of strong shifts of λ_{max} (50–70 nm) toward shorter wavelengths (blue shift). The reasons for such strong and ion-specific blue shifts are discussed elsewhere [27, 28]. The visible spectra of the murexide complexes with Ag^+ and Hg^{2+} are quite rare (Fig. 1).

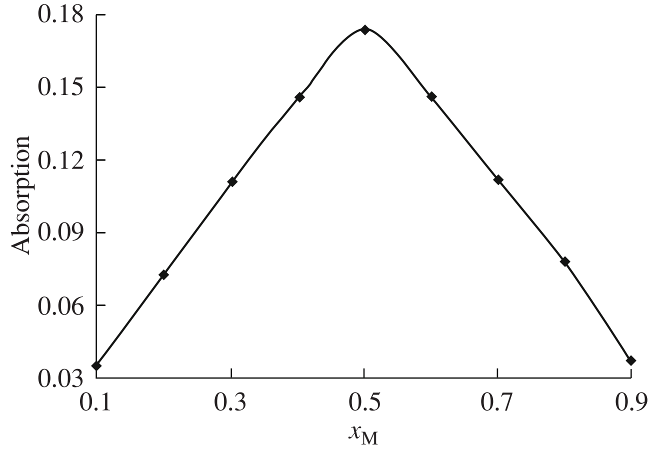


Fig. 3. Continuous variation plot for Ag^+ ion (4.0×10^{-5} M) with murexide (4.0×10^{-5} M) in the presence of DBPY18C6 (1×10^{-2} M) in DMSO at 25°C (x_M mole fraction of Ag^+).

The absorption spectra of murexide in DMSO upon titration with increasing amount of different metal ions in the absence and presence of DBPY18C6 were also obtained. A sample spectrum for the murexide–Hg^{2+}complex in the presence of DBPY18C6 is shown in Fig. 2. The stoichiometry of murexide complexes were examined by mole ratio method and supported by the computer fitting program. In all cases, the stoichiometry was found to be 1 : 1, which was confirmed by a well defined isosbestic-point in the resulting spectra (Fig. 2). Further effort by performing the continuous variation method emphasizes the simple 1 : 1 stoichiometry of the complexation reaction, and the plot of Ag^+–murexide in the presence of DBPY18C6 in DMSO solution is shown in Fig. 3. This stoichiometry in a more polar solvent such as DMSO with Gutmann DN = 29.8 is quite expected [26, 29, 30].

The monitoring of complex formation of DBPY18C6 toward used metal ions in the presence of murexide has been performed. For this purpose, an aliquot solution of both DBPY18C6 and murexide in DMSO was titrated with a concentrated metal ion solution by using a precalibrated syringe. The absorbance measurements at λ_{max} of the metal ion–murexide complex have been done. Attainment of equilibrium was checked by the observation of no further change in the spectrum after several hours. The sample absorbance–mole ratio plots in the absence and presence of crown are shown in Fig. 4. The formation constants of 1 : 1 complexes of the used metal ions and DBPY18C6 in the presence of murexide have been estimated as mentioned above. So far, all equilibria, which exist in the system, were discussed as following.

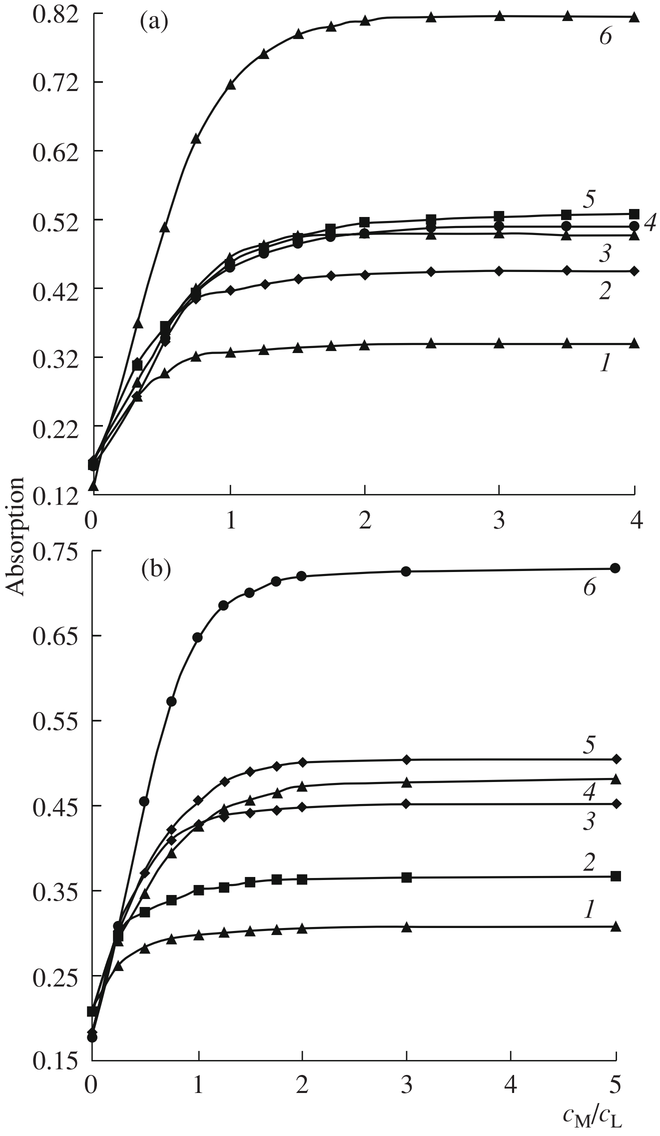


Fig. 4. Absorbance-mole ratio plots for 4.0×10^{-5} M murexide (a) and 4.0×10^{-5} M murexide in the presence of DBPY18C6 (1×10^{-2} M) (b) with 4.0×10^{-3} M solutions of Ag^+ (*1*), Pb^{2+} (*2*), Cu^{2+} (*3*), Cd^{2+} (*4*), Co^{2+} (*5*), and Zn^{2+} (*6*) in DMSO solutions at 25°C.

When a metal ion (**M^{n+}**) reacts with Mu and Crown to from 1 : 1 complexes, the corresponding formation constants can be written as

$$M + Mu = Mmu, K_{MMu} = [MMu]/[M][Mu]; \quad (1)$$

$$M + Crown = MCrown; \quad K_{MCrown} = [M_{Crown}]/[M][Crown] \quad (2)$$

(charges are omitted for simplicity). Mass balance equations and the observed absorbance (**A_{obs}**) are given as

$$c_{Mu} = [Mu] + [MMu], \quad (3)$$

$$c_{Crown} = [Crown] + [MCrown], \quad (4)$$

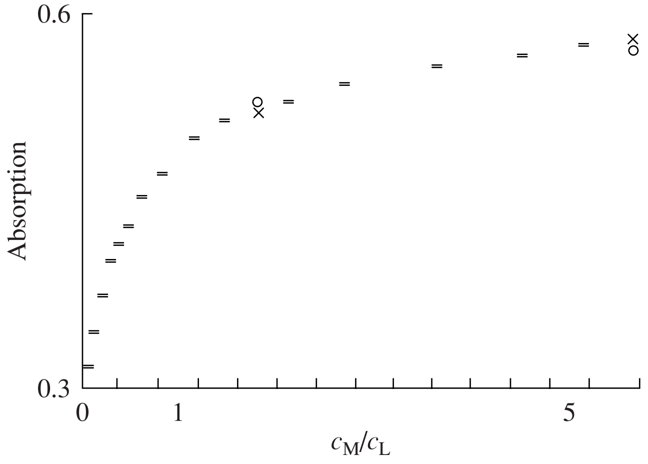


Fig. 5. Sample computer fit of absorbance vs. Hg^{2+}: murexide mole ratio plot in the presence of DBPY18C6 (1×10^{-2} M) in DMSO solutions at 25°C: (×) – experimental point; (o) – calculated point. $c_{Hg^{2+}} = 4.0 \times 10^{-3}$, $c_{murexide} = 1 \times 10^{-2}$ M.

$$c_M = [M] + [MMu] + [MCrown], \quad (5)$$

$$A_{obs} = \varepsilon_{Mu}[Mu] + \varepsilon_{MMu}[MMu], \quad (6)$$

where c and ε values are the analytical concentration and molar absorptivity of the species indicated, respectively. The mass balance equations can be solved in order to obtain an equation for the free metal ion concentration [M] as follows:

$$\begin{aligned} & K_{MMu}K_{MCrown}[M]^3 + \{K_{MMu}K_{MCrown}(c_M - c_{Mu} \\ & - c_{Crown}) - K_{Mmu} - K_{MCrown}\}[M]^2 - \{K_{MCrown} \\ & \times (c_M - c_{Crown}) + K_{MMu}(c_{Mu} - c_M) - 1\} \\ & \times [M] - c_M = 0. \end{aligned} \quad (7)$$

For evaluation of the formation constants from the absorbance vs. c_M/c_{Mu} mole ratio data, the non-linear least-squares curve fitting KINFIT program was used [31]. Since the KINFIT program is robust for model selection, it was used to support the stoichiometry of resulted complexes of both murexide–metal ion, crown ether–metal ion and computation of the stability constants [31]. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [32] or the Powell procedure [33]. Adjustable parameters are the formation constants K_{MMu} and K_{MCrown} and molar absorptivities ε_{Mu} and ε_{MMu}. The free metal ion concentration was calculated from (7) by the Newton-Raphson procedure [34]. Once the value of [M] had been obtained, the concentrations of all other species involved were calculated from the mass balance equations (3)–(5), using the estimated values of the formation constants and molar absorptivities of the current iteration step of the program. Refinement of the param-

Logarithms of stability constants ($\log K_f \pm \sigma$) for some transition and post-transition metal ion (M^{n+}) for resulting complexes with murexide (Mu) and DBPY18C6 in DMSO solution at 25°C

Cation	λ_{max}, nm[a]	Ionic size[b]	$\log K_{MMu}$	$\log K_{MMu}^{c, d}$	$\log K_{M-DBPY18C6}$	$\log K_{M-DBPY18C6}^{e}$
Co^{2+}	466	0.75	4.70 ± 0.06	4.64 ± 0.06^c	2.62 ± 0.01	
Cu^{2+}	477	0.77	5.90 ± 0.03	5.83 ± 0.08^c	3.31 ± 0.01	3.05 ± 0.04
Zn^{2+}	457	0.74	4.60 ± 0.05	4.53 ± 0.07^c	2.78 ± 0.01	2.98 ± 0.10
Cd^{2+}	487	0.95	4.90 ± 0.03	4.79 ± 0.05^c	3.21 ± 0.01	2.85 ± 0.10
Pb^{2+}	515	1.19	4.70 ± 0.03	4.52 ± 0.03^d	3.46 ± 0.01	5.14 ± 0.05
Ag^{+}	522	1.15	3.50 ± 0.08		3.85 ± 0.02	5.64 ± 0.01
Hg^{2+}	507	1.19	3.15 ± 0.02		3.15 ± 0.01	

Note: [a] λ_{max} for murexide is 530 nm; [b] ionic size [35]; [c] in DMSO at 25°C [30]; [d] in DMSO and water at 25°C [26]; [e] in methanol as solvent at 25°C [14].

eters was continued until the sum-of-squares of the residuals between calculated and observed values of absorbance for all experimental points was minimized. The output of the KINFIT program comprises refined parameters, the sum-of-squares, and the standard deviation of data.

All the resulting formation constants, evaluated from computer fitting of the absorbance-mole ratio data, are listed in table. A sample computer fit of the data is shown in Fig. 5. Our assumption of 1 : 1 stoichiometry for the murexide and DBPY18C6 complexes with Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, and Hg^{2+} seems reasonable in the light of the fair agreement between observed and calculated absorbances. These results have good agreement with traditional methods such as mole ratio plots (Fig. 4) and also continues the variation plot (Fig. 3). The sequence of stability of the murexide complexes with the transition metal ions varies in order $Co^{2+} < Cu^{2+} > Zn^{2+}$ and with post-transition metal ions $Cd^{2+} > Pb^{2+} > Ag^+ > Hg^{2+}$, the obtained results are shown in table. These results show that the sequence of stability of the murexide complexes with transition metal ions ($Co^{2+} < Cu^{2+} > Zn^{2+}$) follows the Irving–Williams order [36], which generally holds for stability constants of transition metals. However, among cations Zn^{2+}, Cd^{2+}, and Pb^{2+}, the cadmium–murexide complex in DMSO has the higher stability. This probably due to the proper size of Cd^{2+} ion, which could favor a suitable spatial fit with flexible donated atoms of ligand (bridging nitrogen atom and neighboring oxygen atoms murexide, and **I**) [27, 28]. Increase in the radius of metal ion causes the torsion angle between two rings, which correlated with an increase in wavelength and decrease in the absorbance of spectrum from 466 (Co^{2+}) to 522 nm (Ag^+) Fig. 1 [27, 28]. The nicely correlation between the blue shift in the spectra by increasing radius of metal ion is also seen in table.

The obtained results in table, also clearly show the stability of resulting DBPY18C6 complexes varying in the order $Ag^+ > Pb^{2+} > Cu^{2+} > Cd^{2+} > Hg^{2+} > Zn^{2+} > Co^{2+}$. The ionic size of Co^{2+} (1.13), Zn^{2+} (1.48), Cd^{2+} (1.90), and Cu^{2+} (1.54 Å) ions [36] are too small for the cavity of DBPY18C6 (2.68–2.86 Å) [17] and, thus, it is not surprising that the resulting complexes are weaker. Increasing the stability of the Cu^{2+} complex over the Zn^{2+} complex follows the Irving–Williams order [36], which generally holds for the equilibrium constants of first series of transition metals [30]. In DBPY18C6, the presence of three aromatic moieties in this macrocycle substantially reduced the affinity of the donor atoms toward the transition metal ions. The presence of pyridino nitrogen as a "soft" base has low tendency to interact with relatively "hard" cations [37]. Therefore, moderate stability constants for complexation of DBPY18C6 with transition metal ions are quite expected. In the series of post-transition metal ions Ag^+(2.30), Pb^{2+}(2.38), and Hg^{2+}(2.38 Å), the size of all these cations are proper to fit in the cavity of DBPY18C6, but the charge and solvent effect has the main roles in interaction with this 18C6 ring. It is interesting to note that the bivalent Pb^{2+} and Hg^{2+} ions have approximately the same ionic size as the univalent Ag^+ ion, and it is expected to form more stable complex with DBPY18C6. Pb^{2+} and Hg^{2+} form a relatively weaker complex than Ag^+ does. Such an unexpected stability of the Ag^+ complex could be partly due to the stronger interaction of the pyridino nitrogen of the ligand as a soft base with the Ag^+ ion as a softer acid than Pb^{2+} and Hg^{2+} [37–39]. On the other hand, the solvent influences assisted to this route. DMSO is a solvent with high solvating ability (DN = 29.8), which removes difficulties associated with metal ion hydrolysis and can strongly compete with murexide and DBPY18C6 for metal ions and causes low stability constants of resulted complexes. It is well known that the Gutman donating ability of solvent [29] plays a key role in different complexation reactions [16, 21–24]. In another view the solvating ability of DMSO toward the soft metal ion such as Ag^+, Hg^{2+}, and Pb^{2+}, because of the presence of sulfur in its structure is higher than that of methanol. So, DMSO has a serious competitive role in complexation of these metal ions with DBPY18C rather than methanol (DN = 19.0 [39, 40]). In the series of Ag^+, Hg^{2+}, Pb^{2+}, univalent ions, such as Ag^+, which are weakly solvated, the cation size can be considered primarily responsible for the complexing characteristics. Bivalent cations such as Pb^{2+} and Hg^{2+} are strongly solvated. Therefore, considerably more energy must be expended in the desolvation step of bivalent rather than for univalent cations. Contributions of the solvent–complex and even solvent–ligand interactions on the stability of the resulting complexes cannot be ignored [41, 42]. Moreover, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, as can be understood from 'ion-in-the-hole' model [17], but a measure of the relative strength as compared to the ionic solvation. Thus, for transition metal ions, which have no proper size for including into the ring of DBPY18C6 and has stronger solvation in DMSO, moderate stability constants are quite expected.

Recently, we have compared the chemical behaviors of DBPY18C6 in a series of 18-crown–6 complexation reactions with alkaline-earth cations in methanol by competitive potentiometric method and shown that the stability constant varied in the order DCY18C6 > 18C6 > DB18C6 > DBPY18C6 (logarithm of stability constant of DBPY18C6 with $Ca^{2+} = 3.04 \pm 0.03$, $Sr^{2+} = 4.03 \pm 0.02$, $Ba^{2+} = 4.64 \pm 0.01$ [15]). We also compared the complexation reaction of DBPY18C6 with other 18-crowns–6 toward La^{3+} ions by competitive spectrophotometric method in DMSO solution and shown that the sequence of resulted complexes varies as 18C6 > DCY18C6 > DB18C6 > DBPY18C6 (logarithm of stability constant of DBPY18C6 with $La^{3+} = 1.94 \pm 0.01$, $Ce^{3+} = 1.89 \pm 0.01$, $Pr^{3+} = 1.68 \pm 0.01$, and $Er^{3+} = 1.62 \pm 0.01$ [16]).

Comparison of obtained results in this study with our pervious works shows good agreement and is seen in table. The solvating ability of DMSO rather than methanol for Ag^+ and Pb^{2+} are clearly found from illustrated results. Some variations are seen, which may be due to various accuracy and reproducibility of different experimental techniques and used conditions, such as solvent, electrolyte, and ionic strength [39, 43].

Thus, we conclude that the main parameters for specificity and affinity of the complexation reaction of DBPY18C6 with some transition and post-transition metals are substituted pyridyl unit into 18-membered ring, size of cations, chemical behavior of them, and solvating ability of DMSO, which were considered. The obtained results for complexes of DBPY18C6 and murexide with Ag^+ and Hg^{2+} in DMSO are novel and interesting.

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