ORIGINAL ARTICLE

Spectrophotometric and conductometric studies of the thermodynamics complexation of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} ions with 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane ligand in acetonitrile solution

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Abstract The complexation reaction between 1,13-bis (8-quinolyl)-1,4,7,10,13-pentaoxatridecane ligand (Kryptofix5) and Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} ions were studied conductometrically in acetonitrile solution. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance and absorbance measurements in various mole ratios. The enthalpy and entropy changes of the complexation reactions were derived from titration conductometry in acetonitrile at various temperatures. At 25 °C, the stability of the resulting complexes varied in the order $Pb^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$.

Introduction

Since the first report of Moore and Pressman on the induction of the transport of potassium ions through the mitochondrial membrane by the antibiotic valinomycin [1], a series of other naturally occurring and synthetic compounds (including crown ethers and cryptands) has been discussed as potential ion carriers in artificial and biological membranes. Due to the similarities of open-chain polyethylene glycols in many respects to synthetic and naturally occurring antibiotics, there has been a growing interest in the coordination chemistry of these ligands and their metal ion complexes. However, in comparison with the macrocyclic crown ether and cryptands, much less thermodynamic data is available on the complexation of open chain polyethylene glycols.

Voegtle et al. investigated the complexation of Kryptofix5 (Fig. 1) and another open-chain quinoline polyether with alkali metal ions in methanol by absorption measurements [2] and then reported thermodynamic parameters of complexation for Kryptofix5 and alkali metal cations in methanol at 25 °C [3]. Competitive spectrophotometric method for the complexation studies of alkali, alkaline earth and transition metal ions with Kryptofix5 have been reported [4].

Recently the interaction of Kryptofix5 with alkali metal cations (Li^+, Na^+ and K^+) in aprotic medium (acetonitrile) has been investigated [5].

It was of interest to us to study the interaction of transition and heavy metal ions with this ligand because it has been less reported in the literature. Consequently in the present study, we report our results of the complexation study between Kryptofix5 and Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} cations in acetonitrile by conductometry and spectrophotometry methods.

Heavier main group elements like Pb(II), in complex compounds, generally exhibit a stereochemically active lone pair when the donor atoms are nitrogen, oxygen or fluorine [6]. The lone pair effect has been attributed to the effect of the "inert electron pair" and originates from a combination of shell structure and relativistic effects [7].

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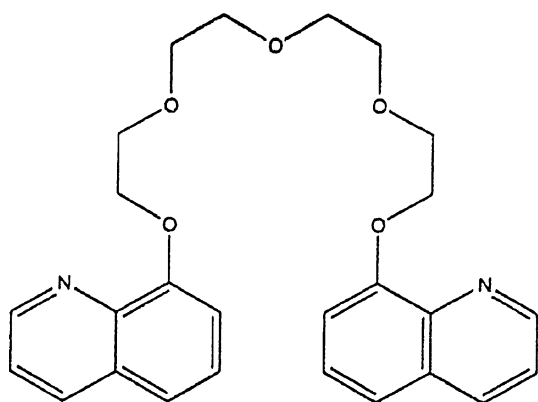Department of Chemistry, Payame Noor University, Ardakan, Iran

Fig. 1 The1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane ligand (Kryptofix5)

Because of this effect, the element lead can be viewed as a relativistic alkaline earth metal. Therefore it is important to be investigated the complexation of Pb(II) with Kryptofix5 including nitrogen and oxygen donor atoms and compare its tendency for Pb(II) with common transition metal cations such as Zn(II), Cu(II), Ni(II) and Co(II). In addition, it is important to be studied the ability of Kryptofix5 in removing of this metal cations especially the toxic metal of lead.

Experimental

Reagents

Reagent grade Kryptofix5 and nitrate salts of Cobalt, Copper, Zinc, Nickel and Lead (all from Merck), were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade acetonitrile (Merck) was purified and dried by the previously described method [8]. The conductivity of the solvent was $<1 \times 10^{-7}$ S cm^{-1}.

Spectrophotometric titrations

All UV–Vis spectra recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10 mm quartz cell. Absorption measurements were carried out with a single-beam Jenway 6305 spectrophotometer equipped with a Jenway Heated Cell Block Controller. 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 Hamilton syringe. The absorbance of the solution was measured after each

addition. The metal ion solution was continually added until the desired metal to ligand mole ratio was achieved.

Conductometric titrations

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 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 Kryptofix5 ligand in acetonitrile (5.0×10^{-3} mol L^{-1}) was added in a stepwise manner using a Hamilton syringe. The conductance of the solution was measured after each addition. The Kryptofix5 ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

In all measurments, cell was thermostated at desired temperature $\pm$ 0.1 °C; the cell constant at the different temperature used was determined by measuring the conductivity of 1×10^{-2} mol L^{-1} solution of analytical grade KCl in triply distilled deionized water. The specific conductances of this solution at various temperatures have been reported in the literature [9]. The corresponding cell constant at 15, 25, 35, and 45 °C were 0.834, 0.832, 0.829 and 0.820 cm^{-1} respectively. A dip-type conductivity cell made of platinum black.

Stability constants of metal ions-ligand system

The formation constant (K_f) and the molar absorptivity (ε) of the resulting 1:1 complexes between the Kryptofix5 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 [10, 11], 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 [12].

For evaluation of the formation constant from molar conductance versus 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 [13].

Thermodynamic parameters of metal ions-ligand system

In order to have a better understanding of the thermodynamics of complexation between Kryptofix5 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 ML complexes as a function of temperature with Van't Hoff Equation (Eq. 1).

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

Results and discussion

Spectrophotometric studies

The electronic absorption spectra of Kriptpfix5 ligand and its Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} complexes in acetonitrile are shown in Fig. 2, and for Pb^{2+} in the increasing concentration of cations were recorded in acetonitrile at 25 °C (Fig. 3). The resulting complexes of Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} with Kryptofix5 are distinguished by a spectral shift of about 25 nm toward longer wavelength, and for Zn^{2+} about 30 nm toward shorter wavelength in comparison to the free ligand. The stoichiometry of the metal complexes was examined by the mole ratio method. Sample of the resulting plots are shown in Fig. 4 at 330 nm, and it is evident that 1:1 (metal ion to ligand) complexes are formed in solution.
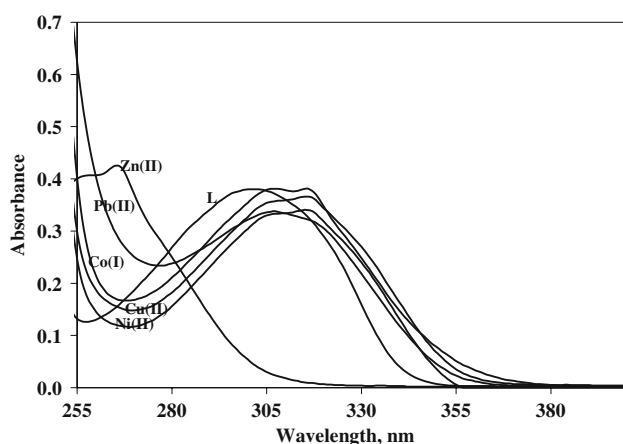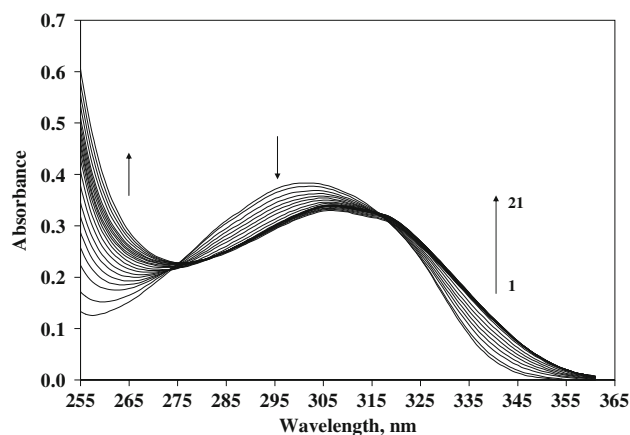
Fig. 3 Electronic absorption spectra of Kryptofix5 ligand (5×10^{-5} mol L^{-1}) in the presence of increasing concentration of Pb^{2+} ions at 25 °C. The molar ratio of $[Pb^{2+}]$/[L] from down to up equal to: 0.0, 0.13, 0.26, 0.39, 0.52, 0.65, 0.78, 0.91, 1.04, 1.17, 1.30, 1.43, 1.56, 1.69, 1.82, 1.95, 2.08, 2.34, 2.60, 2.86, 3.12
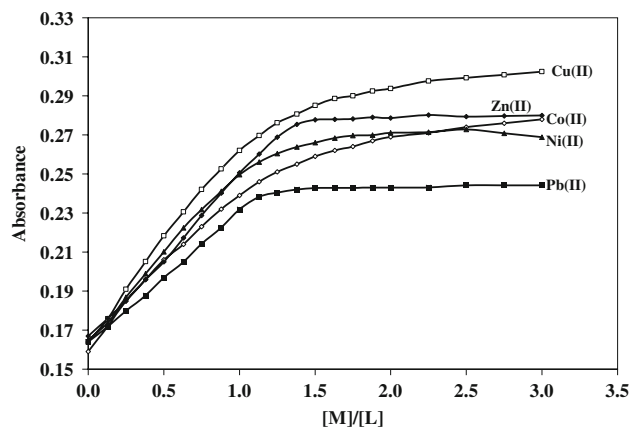
Fig. 4 Mole ratio plots of the Kryptofix5 ligand (5.0×10^{-5} mol L^{-1}) with metal ions at 330 nm at 25 °C

The formation constants of the resulting 1:1 metal ions to Kryptofix5 complexes were obtained at 25 °C by absorbance measurements of solutions in which various concentrations of metal ions were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of Kriptofix5 solution, at 330 nm. All the resulting absorbance-mole ratio data were best fitted to Eq. 2, which further supports the formation of ML in solution.

$$K_f[L]^2 + (1 + K_f C_M - K_f C_L)[L] - C_L = 0 \qquad (2)$$

For evaluation of the formation constants and molar absorptivity coefficients from absorbance versus [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 Kryptofix5 at 25 °C is shown in Fig. 5. The resulting K_f of the Kryptofix5 complexes at 25 °C are listed in Table 1. The
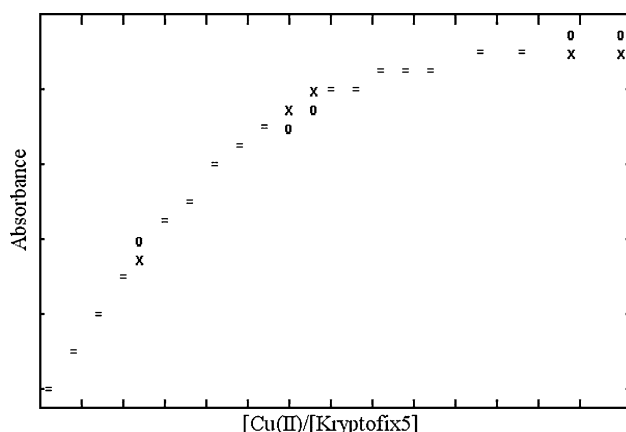
Fig. 2 Spectra of Kryptofix5 ligand and its complexes with Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ions

Fig. 5 Computer fit of absorbance versus [Cu^{2+}]/[Kryptofix5] mole ratio plot in AN at 25 °C, (X) experimental point, (O) calculated point, (=)experimental and calculated points are the same within the resolution of the plot

Table 1 Spectrophotometric formation constants for M^{2+}-Kryptofix5 complexes at 350 nm

Cation (Ionic radius Å)[a]	Log $K_f \pm$ SD[b]
Pb^{2+} (1.19)	5.20 ± 0.01
Zn^{2+} (0.74)	5.13 ± 0.01
Cu^{2+} (0.73)	5.12 ± 0.01
Co^{2+} (0.745)	5.01 ± 0.01
Ni^{2+} (0.69)	4.85 ± 0.01

[a] SD = Standard deviation

[b] Ref. [22]

data given in Table 1 revealed that, at 25 °C, the stability of the 1:1 complexes of the Kryptofix5 ligand with different cations decrease in the order Pb^{2+}>Zn^{2+} > Cu^{2+}> Co^{2+}> Ni^{2+}.

Conductometric studies

The molar conductance of the nitrate salts of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+}in acetonitrile solvent was monitored as a function of the Kryptofix5 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 all metal ions at 25°C is shown in Fig. 6 and for Pb^{2+} and Cu^{2+} ions complexes at different temperatures is shown in Fig. 7. It is evident that ML complexes are formed in solution. 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 increase 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 [14–16]. This might indicate that the
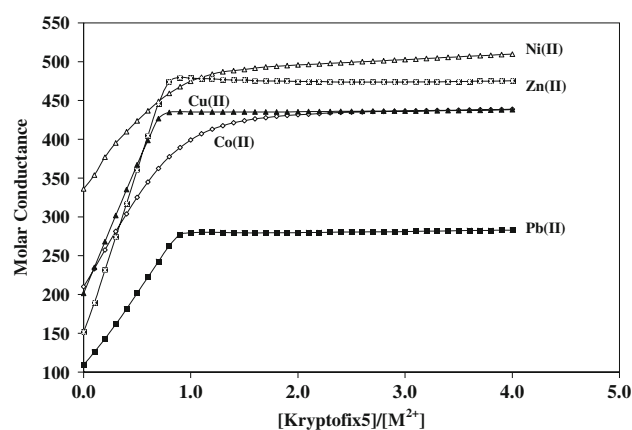

Fig. 6 Molar conductance-mole ratio plots of the metal ions (5.0 × 10^{-5} mol L^{-1}) with Kryptofix5 ligand (5.0 × 10^{-3} mol L^{-1}) at 25 °C
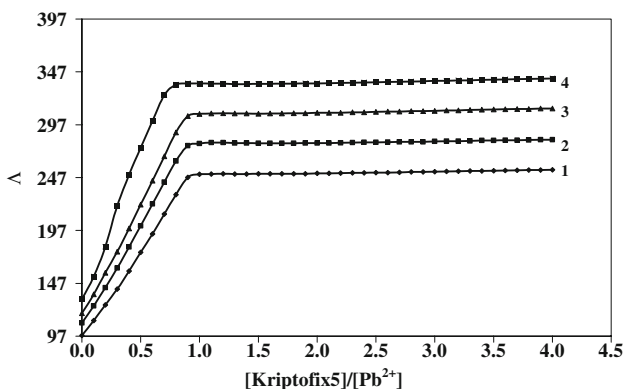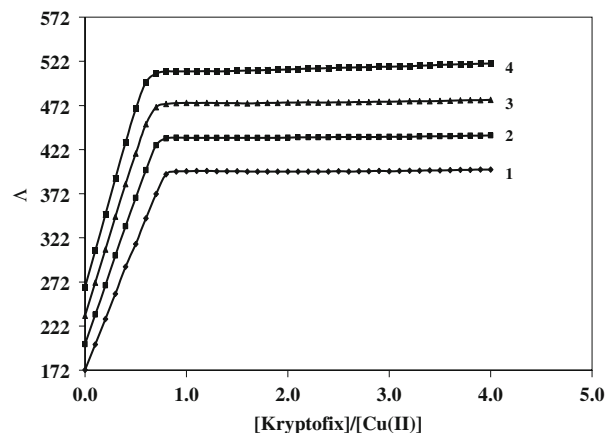

Fig. 7 Mole ratio plots of Kryptofix5 and it's complexes with Cu^{2+} and Pb^{2+} ions at various temperatures: (1) 15 °C, (2) 25 °C, (3) 35 °C, (4) 45 °C

complexes formed are more mobile than the solvated metals ions.

The first addition of Kryptofix5 ligand will complex with metal 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
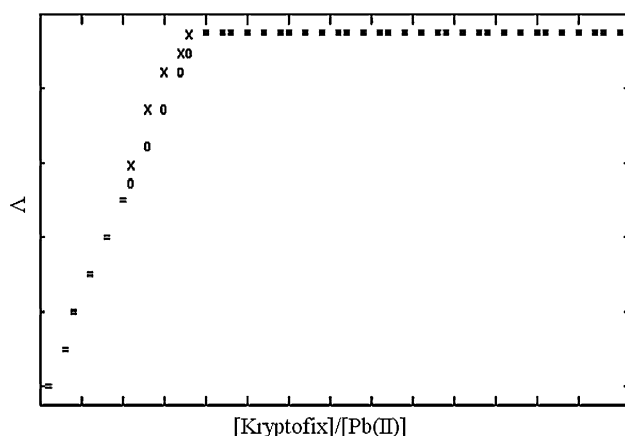
Fig. 8 Computer fit of molar conductance versus [Kryptofix5]/[Pb^{2+}] mole ratio plot in acetonitrile at 25 °C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

in conductivity. However, the slope of the corresponding molar conductance-mole ratio plots change at the point where the ligand to ions ratio is 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 complexes in solutions.

The formation constants of the resulting ML complexes were obtained by molar conductance measurements of solutions in which various concentrations of ligand (5.0×10^{-3} mol L^{-1}) were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of metal ions solution. The entire resulting molar conductance-mole ratio data were best fitted to Eq. 2, which further supports the formation of ML complexes in solution.

For evaluation of the formation constants from molar conductance versus C_L/C_M mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the molar conductance-mole ratio data for Pb^{2+} and Kryptofix5 at 25 °C is shown in Fig. 8. The resulting K_f of the Kryptofix5 complexes at 25 °C are listed in Table 2.

All of the $logK_f$ values evaluated from the computer fitting of the corresponding molar conductance-mole ratio data are listed in Table 2. Van't Hoff plots of $logK_f$ vs. 1/T, for metals complexes in acetonitrile were linear and are shown in Fig. 9. ΔH^0 and ΔS^0 values were determined from Van't Hoff Equation (Eq. 1) in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in Table 2.

Comparison of the data given in Table 2 indicates that the stability of the ML complexes to vary in the order $Pb^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. Pb^{2+} ion fits well into the sterically optimum cavity of ligand Kryptofix5. Thus, the favored stability of the Pb^{2+} complex of ligand Kryptofix5 is the consequence of the absence of a desta-bilizing loss of entropy [3]. In spite of the small differences in ionic radius of the first transition series, it is interesting that the stability of Zn^{2+} and Cu^{2+} complexes is stronger than the stability of Co^{2+} and Ni^{2+} with Kryptofix5 because the binding of a ligand to a metal depends on the hardness/softness of the cation in addition of its size and charge. This difference has previously been verified in stability constant of some ligands with Cu^{2+} cation than other first transition series that is referred to as the Irving Williams order [17].

The comparison of Tables 1 and 2 indicate that the order of stability of the ML complexes is the same in two methods, conductometrically and spectrophotometrically, however, the values of each formation constant evaluated by two methods, are not the same. In spectophotometric method the considerable shifts to longer wavelengths have not occurred in titration of Kryptofix5 with metal cations (Fig. 2). Therefore, because of the absorbance of Krypto-fix5 in the studied wavelengths (Figs. 3, 4), the values of each formation constant evaluated by spectrophotometric method, are less different from these evaluated by con-ductometric method.

The change of the topology of the ligand from a linear conformation in the uncomplexed state to a helical con-formation in the complex state leads to a large loss of entropy. This is supported by the experiment finding that

Table 2 Formation constants, enthalpies, and entropies for different M^{2+}-Kryptofix5 complexes in acetonitrile using conductometry

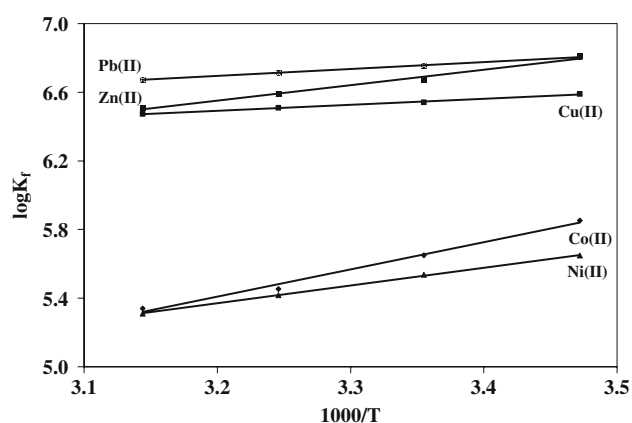| Cation (Ionic radius Å)[a]	Log $K_f \pm$ SD[b]				ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
	15 °C	25 °C	35 °C	45 °C		
Pb^{2+} (1.19)	6.81 ± 0.01	6.76 ± 0.01	6.71 ± 0.01	6.68 ± 0.01	−8 ± 1	103 ± 2
Zn^{2+} (0.74)	6.81 ± 0.01	6.67 ± 0.02	6.59 ± 0.02	6.51 ± 0.02	−17 ± 2	70 ± 6
Cu^{2+} (0.73)	6.59 ± 0.02	6.54 ± 0.02	6.51 ± 0.03	6.47 ± 0.03	−7 ± 0.5	103 ± 1
Co^{2+} (0.745)	5.85 ± 0.02	5.65 ± 0.03	5.45 ± 0.02	5.34 ± 0.03	−30 ± 3	6 ± 9
Ni^{2+} (0.69)	5.65 ± 0.01	5.54 ± 0.02	5.42 ± 0.01	5.31 ± 0.01	−20 ± 0.2	39 ± 1

[a] Ref. [22]

[b] SD = Standard deviation

Fig. 9 LogK$_f$ vs. 1/T for the ML metal ions complexes with Kryptofix5

the decrease of entropy due to complexation is smallest for the uptake of those cations, which do not induce steric deformation of the ligand structure [3].

The changes of the enthalpy of the ligand by complexation are mainly due to the changes of solvation, interamolecular ligand–ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bound metal ion [18].

It is important to discuss these results in terms of the factors which contribute to the selective complexation of macrocycles and metal cations. Among these are the ionic radius of the metal ions, the nature of the donor atoms, the effect of the substituent in the crown ether, and the nature of the solvent.

The ionic radius of the metal ions is expected to play a fundamental role in complexation from the view points of both ionic solvation and ease of binding with the donating oxygen and nitrogen atoms of Kryptofix5. Lead(II) ion has much weaker ionic solvation than do other studied cations. Since complex stability is a balance between the cation–ligand and cation–solvent interactions, the weaker solvation of Pb^{2+} cation will result in stronger complexes with Kryptofix5. Therefore, the selectivity of Kryptofix5 decreases with decreasing of ionic radius (Tables 1, 2).

The thermodynamic data reflect the effect of the donor atoms of the ligand in the complexation process involving the solvent. Thus, the active sites of complexation are provided by nitrogen and ethereal oxygen donor atoms of Kryptofix5. These sites afford a much stronger dipolar interaction as reflected in the higher stabilities of Kryptofix5 with Pb^{2+} in solvent relative to other studied transition metals [19].

Since, in the complexation reactions, the ligand must compete with solvent molecules for cations the use of solvents of low solvating ability is expected to lead greater stability. Because of low stabilities in water and high donicity solvents, we chose to study crown ether

complexation of the metal cations in acetonitrile, a solvent with a moderate dielectric constant (36.64).Moreover, de Nomor et al. have shown that, in acetonitrile, the nitrate anion is not associated with the lead cation complexed by some crown ethers [20].

It is well known that the cryptands due to their high degree of flexibility and increased number of donating atoms in the macrocyclic ring, can wrap themselves around the metal ions of proper size to form tridimensional wrap around complexes, in which all donating atoms of the ring are coordinated to the central cation. In this case, the size of cation is expected to influence strongly the extent of complex formation. The thermodynamic data given in Table 1 show that, in all cases studied, the complexes are enthalpy and entropy stabilized [21].

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