

Conductance and Thermodynamics Study of Interaction of Some Transition Metals with Mixed Oxygen-Nitrogen Donors Macrocycles in Acetonitrile solution

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Received: 10 March 2014;

Accepted: 17 May 2014;

Published online: 10 January 2015;

AJC-16645

The thermodynamic stabilities of the transition metals Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , with the mixed oxygen-nitrogen donor macrocycles, 1,7-diaza-12-crown-4 and 1,10-diaza-18-crown-6, have been determined conductometrically in acetonitrile solution at various temperatures (283, 293, 303 and 313 K). The formation constants, K_f , of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data by using a non-linear least square fitting procedure. The perchlorate salts of these metal ions show a gradual decrease in the molar conductance with addition of the ligand. The binding sequence based on the value of $\ln K_f$ at 298 K, as derived from this study is $Co^{2+} > Mn^{2+} > Cu^{2+} > Ni^{2+}$ for 1,7-Diaza-12-crown-4 for interaction pattern, and $Co^{2+} > Ni^{2+} > Cu^{2+} > Mn^{2+}$ for 1,10-diaza-18-crown-6 interaction. The solvation and the conformational change of the ligands influence the relative stabilities of the complexes. The thermodynamic parameters ΔH° and ΔS° of these interactions were determined from the temperature dependence of the formation constants.

Keywords: Conductometric titration, 1,7-Diaza-12-crown-4, 1,10-Diaza-18-crown-6, Formation constant, Acetonitrile.

INTRODUCTION

The first synthesis of crown ethers, which are macrocyclic polyether having usually the ethylenoxy units as the basic repeating structure, was reported by Pedersen in 1967¹. The ability of these ligands to form strong complexes with metal ions have become a very popular field of research^{2,4}. The complexes are held by electrostatic forces involving ion-dipole interaction between the positively charge cation and the negatively polar oxygen or nitrogen atoms. The stability of metal-ion-crown complexes depends on several factors²⁻⁹ such as: the relative size of the cation (metal ion) and the macrocyclic cavity, the number, kind and arrangement of donor atoms, the ligand substituents, the solvent nature and the counter anion.

Several methods have been used to determine the stability constants of macrocyclic formed. Most of these methods are based on calorimetric titration¹⁰, ion-selective electrode (potentiometric titration)¹¹, spectrophotometric methods⁴ and conductometric methods²⁻⁴ which will be used in this study. Thermodynamic data, enthalpy and entropy, provide much information about the nature of cation interaction with crown ethers.

The coordination chemistry of azacrown ethers (ligand incorporate both oxygen and nitrogen donor atoms) have received intense efforts^{5,8}. Complexes of macrocyclic azacrown ethers with different ring sizes and number of nitrogen atoms have been reported¹²⁻¹⁹. The degree of coordination in the

complexes formed from the interaction of the transition metal ions with the azacrown ethers depend on the nature of the macrocycle, especially the ability of it's backbone to aid or restrict the attainment of particular coordination geometries²⁰.

The stability constants for the 1:1 complexes of the alkali and alkaline earth metal ions with 1,10-diaza-18-crown-6 (D18C6) have extensively been determined in various pure solvents^{5,8}. It was of high interest to study the effect of the cation radius, cation nature on the interaction of metal ions with two crown ethers in pure solvent.

In this work, we report a conductance study of the thermodynamics of Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} ion complexes with 1,7-dioxa-4,10-diazacyclododecane (1,7-diaza-12-crown-4) (L1) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1,10-diaza-18-crown-6) (L2) in acetonitrile solution. The chemical structures of the crown ethers used are shown in Fig. 1.



1,7-Diaza-12-crown-4 (L1)

1,10-Diaza-18-crown-6 (L2)

Fig. 1. Structures of the crown ethers

EXPERIMENTAL

The crown ethers, 1,7-dioxa-4,10-diazacyclododecane (1,7-diaza-12-crown-4) (L1) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1,10-diaza-18-crown-6) (L2), (Fluka) were of high purity (> 96 %) and were used as received. The metal salts used were all of reagent grade, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (BDH) with 98, 97, 95 and 99 % purity, respectively (Fluka). HPLC-grade acetonitrile with 99.6 % purity was purchased from (Gainleind Chemical Company) and was used as a solvent without further purification. The conductivity of the solvent was less than $1 \times 10^{-7} \text{ S cm}^{-1}$ at 25 °C.

The conductance measurements were carried out with a Metrohm-E 518 conductivity meter. The cell constant at the different temperature used was determined by measuring the conductivity of 0.010 mol L⁻¹ solution of analytical grade KCl in triply distilled de-ionized water. The specific conductances of this solution at various temperatures have been reported in the literature²¹. The corresponding cell constant at 283, 293, 303 and 313 K were 0.832, 0.831, 0.828 and 0.823 cm⁻¹, respectively²¹. In all measurements the cell was thermostated at the required temperature ($\pm 0.01^\circ\text{C}$) using Haak-Mess-Technik GmbH U.Co., Type F3 thermostat.

In a typical experiment, 25 mL of the desired metal was placed in the titration cell thermostated to the desired temperature and the conductance of the solution was measured. Then, a known amount of a concentrated crown ether was added in a stepwise manner using a calibrated micropipette.

After stirring the solution magnetically for about 1 min and thermostating it for about 5 min, the conductance was measured after each addition. The same procedure was repeated until the desired ratio of ligand to metal salt was attained.

The formation constants and the limiting molar conductances on 1:1 ratio at various temperatures were evaluated by fitting the observed molar conductance as a function of the free and complexed ions. The formation constants were calculated by using a nonlinear least squares program "simplex" reported elsewhere²².

In order to have a deep insight of thermodynamics of the complexation of metal ions with the studied crown ether (L1 and L2), it is worthy to investigate the enthalpic and entropic contributions in these reactions. The quantities ΔH° and ΔS° of the complexation reactions were calculated from the corresponding $\ln K_f$ and temperature, T, data by applying a linear least square analysis according to the van't Hoff equation:

$$\ln K_f = -\Delta H^\circ / (RT) + \Delta S^\circ / R$$

RESULTS AND DISCUSSION

Transition metals interaction with L1: The molar conductance (Λ), of the hydrated metal perchlorates: $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile at constant salt concentration was monitored as a function of the ligand to metal ion mole ratio at various temperatures. The corresponding plot of the observed molar conductance vs. mole ratio at the temperatures 283, 293, 303 and 313 K is presented in Fig. 2 (initial total metal concentration, $[\text{M}^{2+}] = 5.06 \times 10^{-5} \text{ mol L}^{-1}$. $[\text{L1}] = 1.28 \times 10^{-3} \text{ mol L}^{-1}$).

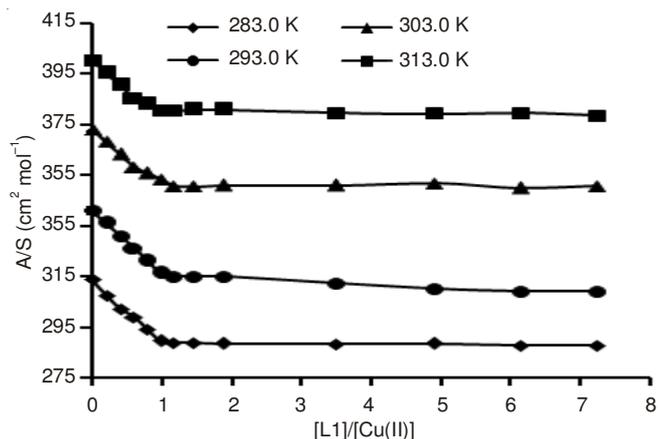


Fig. 2. Λ vs. $[\text{L1}]/[\text{M}]$ curves for L1-Cu (II system at various temperatures

A sample of the resulting plots for all metal ions in acetonitrile at 293 K is shown in Fig. 3.

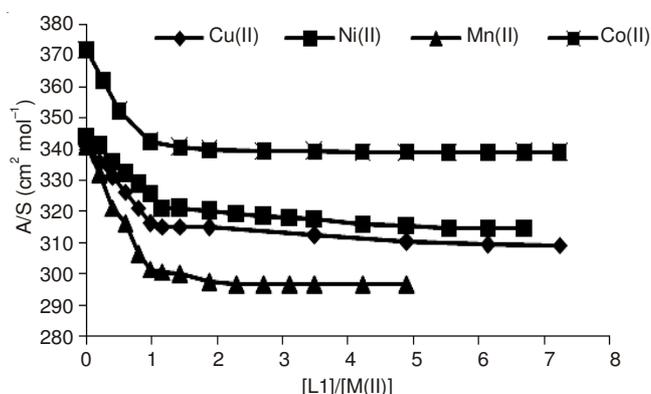


Fig. 3. Molar conductance-mole ratio plot of the metal ions with the ligand L1 at T = 293 K

In all cases, there is a gradual decrease in the molar conductance with the addition of the crown ether and tends to level off at a mole ratio of ligand to metal of about one, which indicates the formation of a relatively stable (1:1) stoichiometry complexes.

The formation constants of (1:1) complexes of crown ethers (L1) with Cu^{2+} , Ni^{2+} , Mn^{2+} and Co^{2+} metal ions at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data are summarized in Table-1.

The plots of $\ln K_f$ vs. $1/T$ for different M^{2+} -L1 macrocycle complexes were linear (Fig. 4). The thermodynamic parameters ΔH° and ΔS° of complexation were determined from the slopes and intercepts of the plots, respectively and presented in Table-1.

The diameter of the metal cations as shown in Table-2 predicts a best match between Ni^{2+} and the ligand (L1) (diameter: 1.20-1.50 Å)²³. But from the values of $\ln K$ in Table-1, the order of stability decrease in the order: $\text{Co}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. It is clear that, the "ion-in-the hole" model has limited usefulness in predicting the stability of the metal ion complexes. However the solvation terms and the crown ether conformational change play a role in determining the stability of the complexes.

The thermodynamic parameters given in Table-1 also shows that Co^{2+} has the most stable interaction due to the

TABLE-1
FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS (ΔH° AND ΔS°) FOR 1:1 COMPLEXES
OF L1 WITH Cu^{2+} , Ni^{2+} , Mn^{2+} AND Co^{2+} IONS IN AN SOLUTION AT DIFFERENT TEMPERATURES

Crown ether	Metal ion	$\ln K_f$				$-\Delta H^\circ$ (kJ/mol)	ΔS° (J/mol K)
		283 K	293 K	303 K	313 K		
L1	Cu^{2+}	11.52 ± 0.01	11.24 ± 0.02	11.22 ± 0.01	10.99 ± 0.02	11.77 ± 2.43	53.91 ± 8.18
	Ni^{2+}	8.95 ± 0.01	8.77 ± 0.02	8.66 ± 0.01	8.61 ± 0.02	8.39 ± 1.34	44.55 ± 4.49
	Mn^{2+}	12.48 ± 0.02	12.12 ± 0.01	12.02 ± 0.01	11.56 ± 0.01	21.02 ± 3.60	29.53 ± 12.1
	Co^{2+}	13.75 ± 0.01	13.66 ± 0.02	13.5 ± 0.02	13.2 ± 0.02	13.22 ± 2.75	68.05 ± 9.25

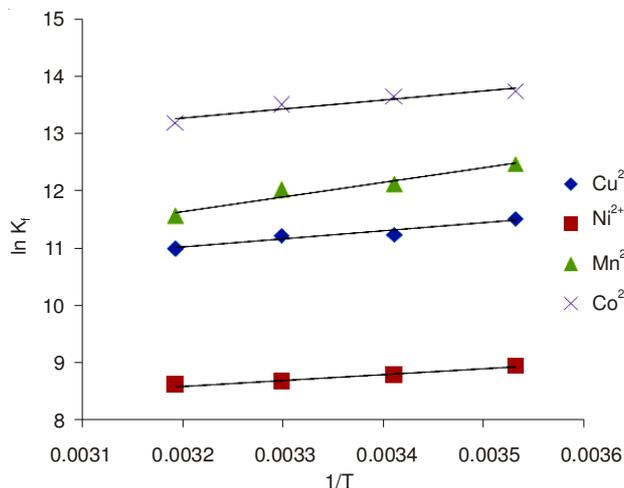


Fig. 4. van't Hoff plots for the 1:1 complexation of L1-M(II)

TABLE-2
DIAMETER OF Mn^{2+} , Cu^{2+} , Co^{2+} AND Ni^{2+} IONS [Ref. 5]

Metal ion	Diameter (\AA)
Mn^{2+}	1.34 (L)
	1.66 (H)
Cu^{2+}	1.54
	1.30 (L)
Co^{2+}	1.50 (H)
	1.26 (L)
Ni^{2+}	1.38 (H)

(L = Low spin, H = High spin)

values of ΔH° and ΔS° [the most negative ΔG° values ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$)].

Transition metals interaction with (L2): The corresponding plots of the observed molar conductance vs. mole ratio at various temperatures (283, 293, 303 and 313 K) are represented in Fig. (5). (initial total metal concentration, $[\text{M}^{2+}]$, = 5.06×10^{-5} mol L^{-1} . $[\text{L}_2] = 1.28 \times 10^{-3}$ mol L^{-1}).

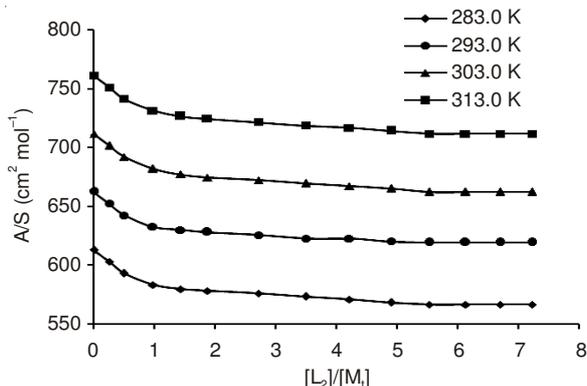


Fig. 5. Λ vs $[\text{L}_2]/[\text{M}]$ curves for Co(II)-L2 system at various temperatures

A sample of the resulting plots for all metal ions in acetonitrile at 293 K is shown in Fig. 6.

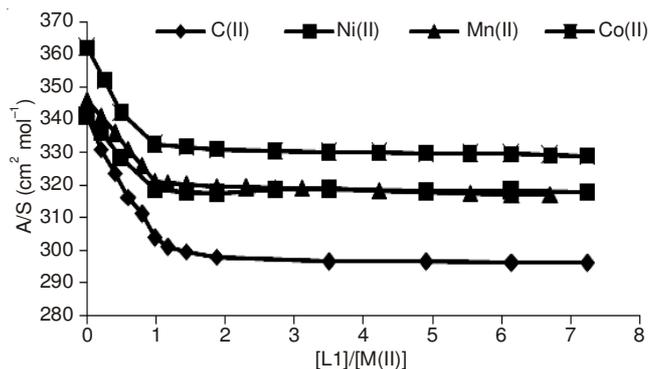


Fig. 6. Molar conductance-mole ratio plots of the metal ions with the ligand L2 at T = 293 K

The formation constants of (1:1) complexes of crown ethers (L2) with Cu^{2+} , Ni^{2+} , Mn^{2+} and Co^{2+} ions at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data are summarized in Table-5.

The plots of $\ln K_f$ vs. $1/T$ for different M^{2+} -macrocycle complexes were linear as shown in Fig. 7.

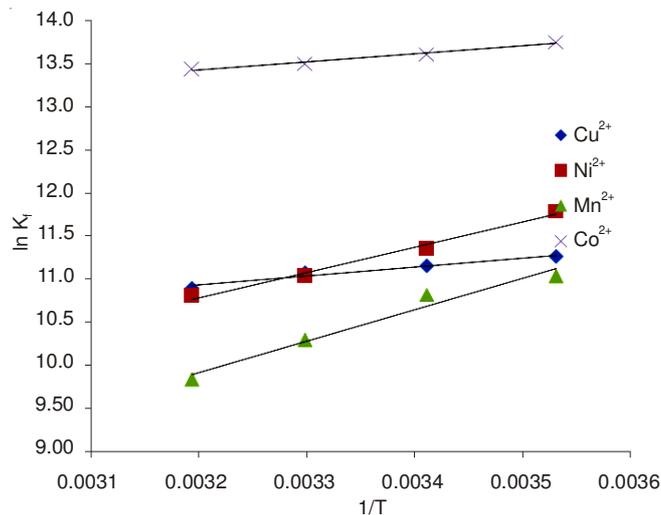


Fig. 7. van't Hoff plots for the 1:1 complexation of L2-M(II)

The thermodynamic parameters ΔH° and ΔS° of complexation were determined from the slopes and intercepts of the plots of $\ln K_f$ vs. $1/T$, respectively and presented in Table-5.

As shown in Figs. 5 and 6, the evidence for the formation of 1:1 complexes of the metal ions with L2 comes from the change in the slope of the corresponding molar conductance ratio plots. According to the values of $\ln K_f$ in Table-5, the

TABLE-3
FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS (ΔH° AND ΔS°) OF 1:1 COMPLEXES OF L2 WITH Cu^{2+} , Ni^{2+} , Mn^{2+} AND Co^{2+} IONS IN ACETONITRILE SOLUTION AT DIFFERENT TEMPERATURES

Metal ion	ln K				$-\Delta H^\circ$ (KJ/mol)	ΔS° (J/mol)
	283 K	293 K	303 K	313 K		
Cu^{2+}	11.26 ± 0.01	11.15 ± 0.02	11.08 ± 0.02	10.89 ± 0.02	8.65 ± 1.39	63.18 ± 4.67
Ni^{2+}	11.79 ± 0.01	11.35 ± 0.02	11.03 ± 0.01	10.80 ± 0.02	24.34 ± 1.94	11.71 ± 6.51
Mn^{2+}	11.03 ± 0.01	10.82 ± 0.01	10.29 ± 0.01	9.83 ± 0.01	30.30 ± 4.10	-14.48 ± 13.79
Co^{2+}	13.75 ± 0.01	13.61 ± 0.02	13.50 ± 0.01	13.43 ± 0.02	7.92 ± 0.65	86.27 ± 2.18

TABLE-4
FORMATION CONSTANTS FOR INTERACTION OF L1 AND L2 WITH Co^{2+} , Ni^{2+} AND Cu^{2+} IN SOLUTION AT 25 °C

Ligand	Metal Ion	ln K	Method	Medium	Ref.	
L1	Co^{2+}	13.27	Potentiometric	H_2O , 0.1 M Et_4NClO_4	24	
	Ni^{2+}	13.61				
	Cu^{2+}	18.79				
L2	Co^{2+}	≥ 8.06	Potentiometric	95 %MeOH, 0.10 M Me_4NCl	25	
		≥ 5.76				H_2O , 0.1 M Et_4NClO_4
	Ni^{2+}	7.48		H_2O , 0.1 M Et_4NClO_4	24	
		≥ 5.76		H_2O , 0.1 M Et_4NClO_4	26	
		≥ 5.76		H_2O , 0.1 M Et_4NClO_4	25	
		7.90		H_2O , 0.1 M Et_4NClO_4	24	
		14.23		H_2O , 0.1 M Et_4NClO_4	25	
		17.48		H_2O , 0.1 M Et_4NClO_4	24	
	Cu^{2+}	6.91		Spectrometric	Me_2SO , 0.1 M Et_4NClO_4	27
		7.60				
		20.20	Potentiometric	95 % MeOH, 0.10 M Me_4NCl	26	

formation constant of the complexes decrease in the following order: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$ with L2 (diameter 2.68-2.86 Å)⁵.

From the diameter of the metals (Table-3) predicts the best match between Mn^{2+} and L2. So that the idea "ion-in-the hole" model can not be the base for the prediction of the stability of interactions between the cations and the ligands always. The ΔH° values in Table-3 show that Ni^{2+} complexes have a more negative than the other complexes, suggesting a stronger binding between the nitrogen donor atoms of L2 and Ni^{2+} .

The formation constants obtained in this study at 20 °C are in satisfactory arrangement with the previously reported values for L1 and L2 presented in Table-4. However, the difference in formation constant values are probably attributed to nature of solvent, temperature, nature and concentration of ionic strength salt.

The low values of ΔH° for some metals, as a result of interaction with L1 and L2, may due to the weak interaction with these ligands, the solvation of the ligands with the solvent acetonitrile and the coordination of ether oxygen to the metal might be considered to be an endothermic process. The Ni^{2+} interaction with L2 is entropy unfavored but the others are favored and there is enthalpy-entropy compensation effect. This can be explained as due to the conformational entropy change and to structural difference between Cu^{2+} and Ni^{2+} complexes. Previous X-ray studies on solid complexes indicated that the copper forms five-coordinate complexes while the nickel forms pseudo-octahedral complexes^{12,16}.

With respect to the Mn^{2+} interaction with L2 is entropy unfavored. The conformational entropy change of the ligand

L2 might have an additional effect. However, the stability of Mn^{2+} complexes is enthalpy governed.

The entropy change of the metal ion-diazacrown systems upon complexation is related to some factors such as the change in the conformational entropy of the ligand and the diameter of crown ether, the extent of crown solvent interaction and the different in the solvation of the free and complexed cation.

In the case of complexation of crown ether ligands, the following factors can significantly influence the stability of their metal ion complexes: (i) the cation size, (ii) the ionic solvation of the charged species involved and (iii) conformations of the free and complexed crown ethers. As shown in Tables 2 and 3, the observed increase (or decrease, depending on the nature of the metal ion and ligand) in ΔH value will be compensated by an increase (or decrease) in the corresponding ΔS value. The existence of such a compensating effect between ΔH and ΔS values has been reported for several ligand-metal system²⁸. This effect causes the overall change in the ΔG value of the complex to be smaller than might be expected from the change in either ΔH or ΔS independently.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Hashemite University, Az Zarqa', Jordan.

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