

COMPETITIVE SPECTROPHOTOMETRIC STUDY OF COPPER, ZINC AND CADMIUM WITH 18C6 USING TAR AS A COLORIMETRIC COMPLEXING AGENT IN METHANOL[☆]

*Rounaghi, Gholam Hossein**

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad,
P.O.Box 91735-654, I.R. Iran

Hosseini, Mohammad Saeed and Ghiamati, Ebrahim

Department of Chemistry, Faculty of Sciences, Birjand University, Birjand, I.R. Iran

ABSTRACT: *A competitive spectrophotometric method has been used for the study of complexation between Cu^{2+} , Zn^{2+} and Cd^{2+} (M) and 18-crown-6(18 C6, B) in methanol using 4-(2-thiazolylazo) resorcinol (TAR, HL) as the colorimetric complexant. Absorption spectra of the species in the M-TAR-18 C6 system at various concentrations of 18C6 showed no formation of ternary complex, MLB, and the stoichiometry of the resulting complexes was found to be 1:1 under the condition used. The formation constants of both types of complexes (ML and MB) were determined using the conditional formation constant of ML complexes at constant acidity in the absence ($K_{ML'}$) and presence ($K_{M'L'}$) of 18C6. The results showed that the K_{MB} values increased in the order of $\text{Cu}^{2+} < \text{Zn}^{2+} < \text{Cd}^{2+}$, the K_{MB} values were comparable with those reported previously.*

KEY WORDS: 18-Crown-6; Cu^{2+} , Zn^{2+} and Cd^{2+} ions; Methanol; Competitive spectrophotometry.

Macrocyclic ligands of the crown ether and cryptand types are capable of forming stable and selective complexes with metal cations [1-3]. The process of ion-macrocyclic association depends on some factors

which are related to characteristic properties of macrocyclic ligand, reacting ion and solvent [2-5]. Perhaps the simplest typical crown ether is 18-crown-6, a stable and commercially available compound which

[☆] Dedicated to Professor Abbas Shafiee on the occasion of his 60th birthday.

* To whom correspondence should be addressed.

1021-9986/98/1/4

4/\$/2.40

is a unique ligand because of its low complexing ability with the small cations, despite their higher charge density. This behaviour for the cations such as Cu^{2+} and Zn^{2+} is very interesting, because a reverse order has been usually noted for most chelating agents [2,3]. Indeed, 18C6 is frequently used as an example of the importance of "size matching" in complexation chemistry. Since the complexation reaction of macrocyclic ligands including 18C6 with some transition metal cations, such as Cu^{2+} , Zn^{2+} and Cd^{2+} has been studied less than other cations, therefore, further studies is necessary for investigation of the stability and selectivity of these metal ion complexes with macrocyclic ligands.

Recently, spectrophotometric procedures involving the competition of the two ligands have successfully been applied to study many complexes [6,7], including some crown ether and cryptand metal ion complexes in nonaqueous solvents [8-14]. In the present work, we have used a previously reported spectrophotometric procedure [14,18] to study the complexation of mentioned cations with 18C6 in methanol, using TAR as a colored competitive ligand. The results are compared with those reported by other researchers. Also, the competitive effect of 18C6 on the selectivity of chelating agent has been explored.

EXPERIMENTAL

Reagents

All chemicals used were of GR grade and were used without further purification. The required quantities of each salt: $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (all from Merck Chemical Co.) were dissolved in methanol (spectroscopic grade from Merck) to prepare solutions with concentration of $12.5\text{--}25 \times 10^{-3}\text{M}$. Each solution was standardized by EDTA titration. 18C6 (Sigma Chemical Co.) was precipitated as its acetonitrile (Merck Chemical Co.) complex [15]. The white crystals were isolated and kept under vacuum at room temperature for 48 hours to remove acetonitrile molecules and then dissolved in methanol. The colored ligand, TAR (Fluka Chemical Co.) solution was prepared with concentration of $1.0 \times 10^{-3}\text{M}$. Perchloric acid (from Merck) and tetraethylammonium perchlorate (from Fluka) were used for adjusting the acidity and the ionic strength of the

solutions, respectively.

Procedure

(a) The metal ion solution was added in successive steps, 10-25 μL each time, using a Hamilton micro-liter syringe to 10.0 mL of a methanol solution containing TAR ($2.0 \times 10^{-5}\text{M}$), at a constant acidity ($1.2 \times 10^{-4}\text{--}12 \times 10^{-5}\text{M HClO}_4$) and ionic strength (0.025), to give a concentration of $(10\text{--}50) \times 10^{-5}\text{M}$.

(b) To the solution prepared by procedure (a) 18C6 solution was further added to give a concentration of $(2\text{--}8) \times 10^{-3}\text{M}$. After each addition of the metal ion, the absorbance was measured at the peak of the complex by using a Shimadzu UV-160A recording spectrophotometer. No precipitation occurred during the experiments.

RESULTS AND DISCUSSION

Absorption spectra

Fig. 1 shows the variation of the absorption spectra of the TAR(HL) solution with varying Cu concentration, $C_{M'}$, at the condition where: $[\text{HClO}_4] = 2 \times 10^{-4}\text{M}$ and $[\text{18C6}] = 0$ (Procedure(a), lines 2,5,6) or $[\text{18C6}] = 4 \times 10^{-3}$ (Procedure(b), lines 3,4). In each procedure, (a) or (b) the absorption of the solutions decreases at the peak of TAR (440 nm) and increases at the peak of TAR-copper complex (568 nm). Moreover, these spectra show a well defined isobestic point (483 nm). This fact indicates that only one colored component except of the colored ligand should be present in the solutions. On the other hand, the use of Mollard method [16] reveals that the colored component is 1:1 Cu-TAR complex, i.e. there is no formation of ternary complex, CuLB. Similar results were obtained for other systems. The observed shift (140 nm) in the absorption spectra of indicator upon addition of metal cation to solutions of TAR (Fig. 1) is due to the formation of metal cation-TAR complex and its equilibrium dissociation. Similar shift has been observed for Y-TAC system [11].

Determination of the conditional formation constant of M-TAR and stability constant of M-18C6 complexes

The measured absorbance A due to M-TAR(HL) complex was used to determine the conditional

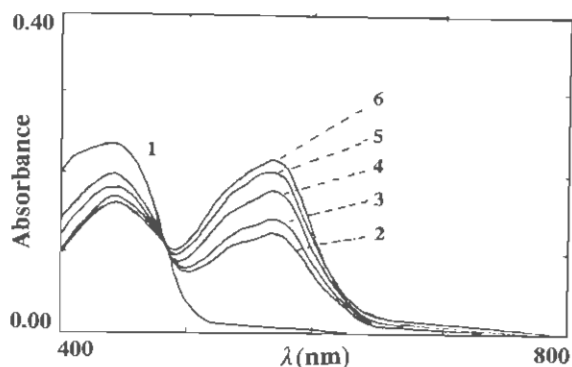


Fig. 1: Spectral changes for Cu-TAR (2,5,6 spectra) and Cu-TAR-18C6 (3,4 spectra; $[18C6] = 4 \times 10^{-3} M$) systems in methanol at $25^\circ C$, $\mu = 0.025$, $[HClO_4] = 1 \times 10^{-4} M$, TAR concentration is $1 \times 10^{-5} M$ and $[Cu^{2+}]$ varies as: (1) $0.0 M$; (2) $2.5 \times 10^{-5} M$; (3) $5.0 \times 10^{-5} M$; (4) and (5) $1.5 \times 10^{-4} M$; (6) $2.0 \times 10^{-4} M$

formation constant at a given acidity, $K_{ML'}$: A was measured at a constant acidity and various concentrations of M in the binary (M -TAR) system [procedure(a)] to obtain the $K_{ML'}$ values, that defined as [17]: $K_{ML'} = [ML]/[M][L']$, where $[L'] = [L] + [HL]$ (the charges are omitted for simplicity). It was determined by the same manner as described in ref. [18]:

$$(A/A_0 - 1)/C_M = \epsilon_{ML} K_{ML'}/\epsilon_{L'} - K_{ML'} A/A_0 \quad (1)$$

where A is the absorbance before addition of metal ion, ϵ_{ML} and ϵ_L are the molar absorptivities of the complex and the free TAR, at a given acidity, respectively.

For ternary M -TAR(HL)-18C6(B) system [procedure(b)], the conditional formation constant at the given acidity, $K_{M'L'}$, is defined as: $K_{M'L'} = [ML]/[M][L']$, where $[M'] = [M] + [MB] + [MB_2]$.

The $K_{M'L'}$ values were determined by a similar equation to (1) (Fig. 2).

$$(A/A_0 - 1)/C_M = \epsilon_{ML} K_{M'L'}/\epsilon_{L'} - K_{M'L'} A/A_0 \quad (2)$$

The values of K_{MB} (Metal-18C6) complexes are obtained from $K_{ML'}$, and $K_{M'L'}$ values using the following equation [11].

$$(K_{ML'}/K_{M'L'} - 1)/C_B = K_{MB} + K_{MB2} C_B \quad (3)$$

A plot of $(K_{ML'}/K_{M'L'} - 1)/C_B$ vs C_B at a relatively low values of C_B and constant acidity, yields a horizontal line for each of the metal ions, Fig. 3; this

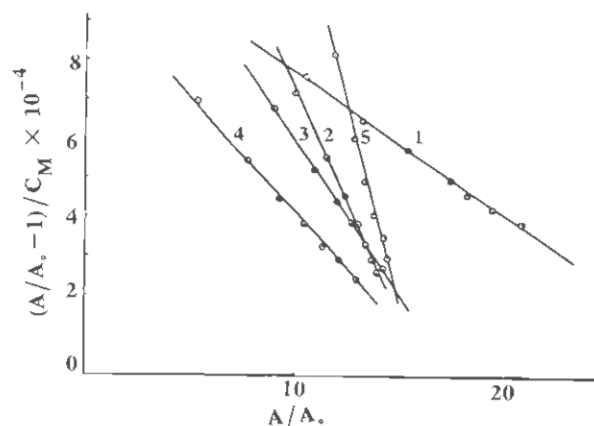


Fig. 2: Plots of $(A/A_0 - 1)/C_M$ vs. A/A_0 for Zn-TAR(1) and Zn-TAR-18C6 systems in methanol. The C_B varies as: (1) $0.0 M$; (2) $0.02 M$; (3) $0.04 M$; (4) $0.06 M$; (5) $0.08 M$.

suggests the formation of 1:1 complexes between the metal ions and 18-crown-6.

Table 1 compares the present and previously reported $\log K_{ML'}$ and $\log K_{MB}$ values. It is obvious that the stability of complexes of the heavy metal cations with 18C6 increases in the order of $Cu^{2+} < Zn^{2+} < Cd^{2+}$.

The response of complex stability to the neutral oxygen donors in crown ethers is a function of metal ion size that gives rise to a rule of ligand design for increasing the selectivity [19]. The molecular mechanics calculations, show that 18C6 has two stable

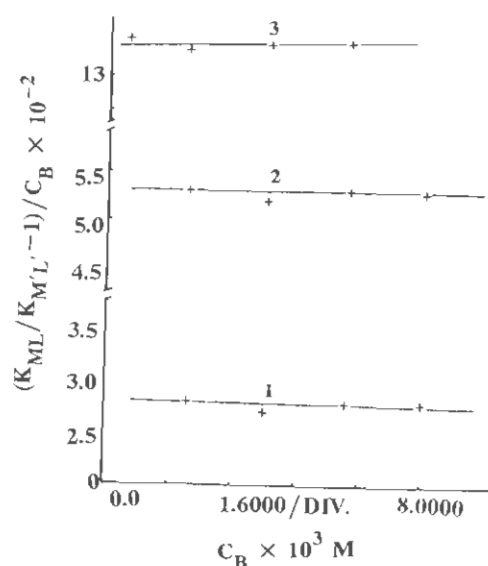


Fig. 3: Plots of $(K_{ML'}/K_{M'L'} - 1)/C_B$ vs. C_B . (1) Cu; (2) Zn; (3) Cd

Table 1: Values of $\log K_f$ of M-18C6 and M-TAR complexes compared to the reported values.

Ligand	Cation	Cation diameter (Å)	$\log K_f$	Medium
18C6	Cu ²⁺	1.14	2.44±0.02	Et ₄ NClO ₄ = 0.025 M
			2.47 ^b	Bu ₄ NClO ₄ = 0.1 M
	Zn ²⁺	1.48	2.72±0.02	Et ₄ NClO ₄ = 0.025 M
			2.22 ^b	Et ₄ NI = 0.1 M
Cd ²⁺	1.90	3.12±0.03	Et ₄ NClO ₄ = 0.05 M	
		3.58 ^c	Et ₄ NClO ₄ = 0.025 M	
TAR	Cu ²⁺		5.19±0.04	HClO ₄ = 2×10 ⁻⁴ M
	Zn ²⁺		3.38±0.03	HClO ₄ = 2×10 ⁻⁵ M
	Cd ²⁺		3.50±0.03	HClO ₄ = 2×10 ⁻⁵ M

$\mu = 0.025$; $t = 25^\circ\text{C}$ in all experiments

a : Ref. 5; b : Ref. 21; c : Ref. 22

conformers with D_{3d} and C_i symmetries [20]. The D_{3d} conformer is required for complex formation, since in this case all of the oxygen atoms participate at the complex structure.

As it is clear from Table 1, the ionic sizes of the metal ions are smaller than 18C6 cavity (2.6-3.2 Å). Because of participation of all of the oxygen donor atoms of the existing ligand at the complex structure, it seems that for these three metal cations, the selectivity of the ligand for large metal ions increases over small metal ions, since in the case of large metal ions, the change in conformation of the ligand upon complexation is less than small metal ions.

Another factor that may influence the stability order of Cu-18C6 and Zn-18C6 complexes could be explained by Pearson theory for hard-soft interactions between Lewis acids and bases. Generally, neutral oxygen donors (ROH, R₂O) act as hard base and more affinity is observed towards hard acids. Since Zn²⁺ is a harder acid than Cu²⁺ (5), it could be expected that the stability constant of Cu-18-crown-6 complex to be higher than Zn-18-crown-6 complex.

ACKNOWLEDGMENT

This work was supported by Birjand University.

Received, 2nd December 1995; Accepted, 18th February 1997

REFERENCES

- [1] Pedersen, C. J., *J. Am. Chem. Soc.*, **89**, 7017 (1967).
- [2] Izatt, R. M., Bradshaw, J. S., Nielsen, S., Lamb, J. D. and Christensen, J., *J. Chem. Rev.*, **85**, 271 (1985).
- [3] Izatt, R. M., Pawlak, K. and Bradshaw, J., *Chem. Rev.*, **91**, 1721(1991).
- [4] Dejong, F. and Reinhoudt, D. N., *Adv. Phys. Org. Chem.*, **17**, 279(1980).
- [5] Hancock, R. D. and Martell, A. E., *Chem. Rev.*, **89**, 1875(1989).
- [6] Ohyoshi, E., *Anal. Chem.*, **57**, 446(1985).
- [7] Ohyoshi, E., *Polyhedron*, **5**, 2101(1986).
- [8] Loyola, V. M., Pizer, R. and Wilkins, G., *J. Am. Chem. Soc.*, **99**, 7185(1977).
- [9] Pizer, R. and Selzer, R., *Inorg. Chem.*, **22**, 1359 (1983).
- [10] Gholivand, M. B., Kashanian, S. and Shamsipur, M., *Polyhedron*, **63**, 535(1987).
- [11] Ohyoshi, E. and Kohata, S., *Polyhedron*, **8**, 1561 (1989).
- [12] Kashanian, S. and Shamsipur, M., *Inorg. Chim. Acta*, **155**, 203(1989).
- [13] Parham, H. and Shamsipur, M., *Polyhedron*, **11**, 987 (1992).
- [14] Alizadeh, N. and Shamsipur, M., *Talanta*, **40**, 503 (1993).
- [15] Gokel, G. M., Cram, D. J., Liotta, C. L., Harris, H. P. and Cobi, F. L., *Org. Synth.*, **56**, 30(1977).
- [16] Ingle, Jr. J. and Grouch, S. R., "Spectrochemical Analysis" Prentice-Hall International, New York (1990).
- [17] Ringbom, A., "Complexation in Analytical Chemistry" Interscience, New York (1963).
- [18] Shamsipur, M. and Alizadeh, N., *Talanta*, **39**, 1209(1992).
- [19] Honcock, R. D., *Pure. Appl. Chem.*, **58**, 3445 (1986).
- [20] Wipff, G., Weiner, P. and Kollman, P. A., *J. Am. Chem. Soc.*, **104**, 3249(1982).
- [21] Chen, L., Grootenhuys, P. D. J., Christenhusz, A., Hoogendem, E., Reinhoudt, D.N. and Vander Linden, W. E., *Anal. Chim. Acta*, **201**, 117(1987).
- [22] Spiess, B., Arnaud-Neu. and Schwing-Weill, M. J., *Helv. Chim. Acta*, **63**, 2287(1980).