

Complexation and thermodynamic studies of oxathiadibenzocrown ethers with Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} ions

M. Ashram · M. Bqaeen · S. Mizyed

Received: 1 July 2009 / Accepted: 3 September 2009 / Published online: 17 September 2009
© Springer Science+Business Media B.V. 2009

Abstract A thermodynamic study of the complexation of Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} ions with **1** and **2** in acetonitrile has been carried out. The study was conducted in the temperature range 283–308 K using a conductometric technique. The observed molar conductivity, Λ , was found to decrease significantly for mole ratios $[\text{L}]_t/[\text{M}]_t$ less than unity in all cases. A model involving 1:1 stoichiometry has been used to analyze the conductivity data. The stability constant, K , for each 1:1 complex was determined from the conductivity data by using a nonlinear least-squares curve fitting procedure. The results show that compound **1** has no peak selectivity for any of the metal cations, while compound **2** selectively associates with Cu^{2+} and Pb^{2+} . Complexes of **1** have the following stability order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ and $\text{Pb}^{2+} > \text{Cu}^{2+}$ for the complexes of **2**. The ΔH° and ΔS° values for the complexation process were obtained from the slope and intercept of the Van't Hoff plots respectively. All ΔG° values were negative and were determined from the Gibbs–Helmholtz equation and the significance of these values is discussed.

Keywords Crown ethers · Oxathiadibenzocrown ethers · Transition metals · Stability constant · Conductivity

Introduction

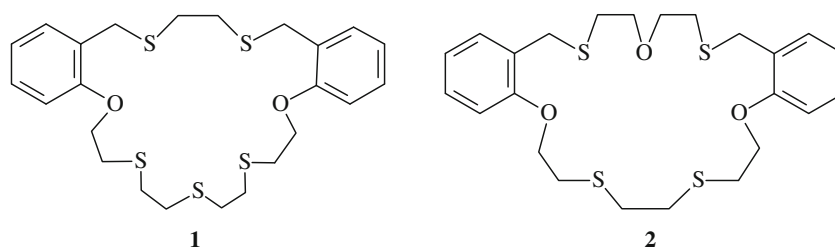
Heavy metals such as cadmium, mercury and lead are toxic substances and required to be removed from environments. One possible way is to extract these harmful metals from water or soil by efficient extractants.

Chemists, play a major role in designing and preparing suitable ligands for this purpose. The complexation ability of a designed ligand for extracting specific metal ions is an important factor to be considered. This can be controlled by a choice of ligating atoms and ring size. The use of crown ethers, that containing hard atoms such as oxygen atoms mainly complex hard metal ions such as alkali and alkaline earth metals, where as those containing soft donor atoms such as nitrogen or sulfur atoms bind transition and heavy metal ions [1]. Another type of crown ethers that designed for chelating transition and heavy metal ions are mixed crown ethers containing different types of soft chelating atoms. The metal ion preferences of mixed donor coordination sites are often difficult to predict especially when transition and heavy metal ions are involved [2]. It was shown that the oxygen bearing, thia, or oxathia crown ethers form stable complexes with soft metal ions [3–10]. Kim et al. synthesized a flexible dibenzo- O_4S_2 -macrocyclic and studied the complexation with Ag^+ . They obtained the X-ray structure of the complex and studied the complexation process in solution by using NMR spectrometry [11]. Demitrieva et al. have synthesized complexes of *cis*- and *trans*-benzodithia-18(21)-crown-6(7) with Pd^{2+} . The X-ray structures of all complexes showed that the soft Pd^{2+} is coordinated to the soft sulfur atoms [12]. The major goal of this project is to synthesize S/O mixed donor crown ethers such as the ones shown in Scheme 1 which were prepared previously [13] and to study their coordination preferences towards metal ions such as, Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} .

M. Ashram (✉) · M. Bqaeen
Chemistry Department, Mutah University, Al-Karak, Jordan
e-mail: ashram_1961@yahoo.com

S. Mizyed
Chemistry Department, Yarmouk University, Irbid, Jordan

Scheme 1 Structures of oxathiadibenzocrown ethers **1** & **2**



Experimental

Materials and experimental procedures

Compounds **1** and **2** were prepared as described in the literature [13]. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), and $\text{Cd}(\text{ClO}_4)_2$ (Aldrich) salts were used without further purification. Acetonitrile (HPLC grade, Phamacos Ltd.) was used as a solvent for crown ethers and the salts. The conductivity of the solvent was less than $1.0 \times 10^{-7} \text{ S cm}^{-1}$. Solutions having metal ion concentrations of approximately $1.00 \times 10^{-4} \text{ M}$ were prepared by dissolving a known mass of each salt in the respective solvent. These solutions were also used as solvents for preparing the crown ethers solutions with concentrations of approximately $1.500 \times 10^{-3} \text{ M}$. Conductivity measurements were carried out with a microprocessor conductivity meter (WTW/LF537) with a calibrated conductivity cell (WTW/Tetracon 96) having a cell constant of 0.618 cm^{-1} . The cell was calibrated using KCl solutions. The temperature of the reaction was controlled by using a thermostated circular water bath with a precision of $\pm 0.1 \text{ }^\circ\text{C}$ (HAAKE D1) equipped with a refrigerating unit. In order to determine the complex formation constants with the studied metal ions, a 50 mL of the desired salt solution was placed in specially designed water jacketed cell (150 mL, pyrex[®]) equipped with a magnetic stirrer and was connected to a thermostated circulator water bath. The conductance of the solutions was measured at each of the thermostated temperature.

Known amounts (0.50 mL) of the solutions of the crown ethers were added in a stepwise manner using a calibrated pipette. The conductivity of the mixture was then measured after stirring and temperature equilibration. This procedure was repeated in the same manner for each addition. Statistical analyses and curve fitting were conducted using a nonlinear least-squares program “Simplex” which was described elsewhere [14].

The variation of molar conductance (Λ_m) versus the ligand to cation molar ratio $[\text{L}]_t/[\text{M}]_t$ for complexation of **1** and **2** the metal cations in acetonitrile was plotted for each system. The stoichiometry for all complexes was shown to be 1:1, and the stability constants were calculated from the variation of the molar conductance as a function of $[\text{L}]_t/[\text{M}]_t$

mole ratio using a nonlinear least-squares program “Simplex” [15].

Results and discussion

In principle, complex formation can be followed by observing changes in physical properties such as heat of reaction, change in colour, conductance or NMR chemical shifts, which can occur as a result of the complexation. Such changes provide information about the stoichiometry and stability of the complex. In this study, complex formation and the thermodynamic parameters were studied by the change in molar conductance.

The variations of molar conductance (Λ_m) versus the ligand to cation molar ratio $[\text{L}]_t/[\text{M}]_t$ for complexation of **1** and **2** with Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} metal cations in AN were studied at $25 \text{ }^\circ\text{C}$. $[\text{L}]_t$ is the total concentration of the ligand and $[\text{M}]_t$ is the total concentration of the metal cation. The detailed mathematical treatment is described elsewhere [15].

In every case the observed molar conductivity, Λ , decreases continuously with the mole ratio $[\text{L}]_t/[\text{M}]_t$ and starts to level off at a mole ratio close to unity as shown in Fig. 1 as an example. This observation indicates the formation of 1:1 complexes of the metal cations and compounds **1** and **2**.

The 1:1 complexes of M^{n+} ($\text{M}^{n+} = \text{Cu}^{2+}$, Pb^{2+} , Zn^{2+} and Cd^{2+}) with triazine macrocyclic compounds also has

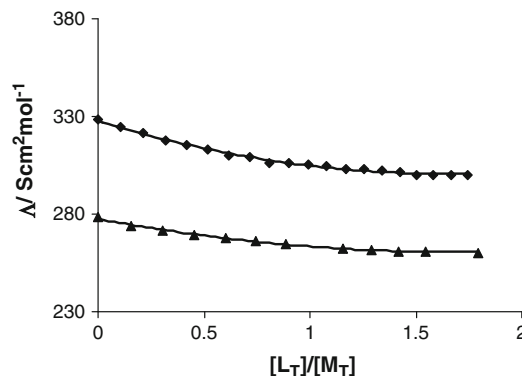


Fig. 1 Plot of Λ versus $[\text{L}]_t/[\text{M}]_t$ for: filled squares $1/\text{Cu}^{2+}$ and filled triangles $1/\text{Pb}^{2+}$ AN at 298 K

been observed by Pourghobadi and Majidi [16]. They studied the complexation of triazine macrocycle with Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} in AN at different temperatures. They found that the slope of the corresponding molar conductivity versus Ligand/Metal cation mole ratio plots changes sharply at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complexes between triazine macrocycle and these metal cations. There was no change on the observed molar conductivity, Λ , accompanied with the addition of **2** solution into Zn^{2+} or Cd^{2+} solutions. This indicates either, there is no complexes are formed between **2** with both cations or the mobility of the complexes of these cations with **2** is similar to the mobility of the metal ions.

The temperature effect on the stability constants was determined. The experiment was repeated at five different temperatures. The thermodynamic quantities ΔH° and ΔS° were calculated from the corresponding Van't Hoff equation and applying a linear least-square analysis. Plot of $\log K$ versus $1/T$ for the compound **1** with Pb^{2+} in AN is shown in Fig. 2 as illustrated example.

Table 1 shows that ΔH° values for the complexation process are negative except for **1**- Cd^{2+} complex, and thus the complexation is as expected enthalpy driven. ΔS°

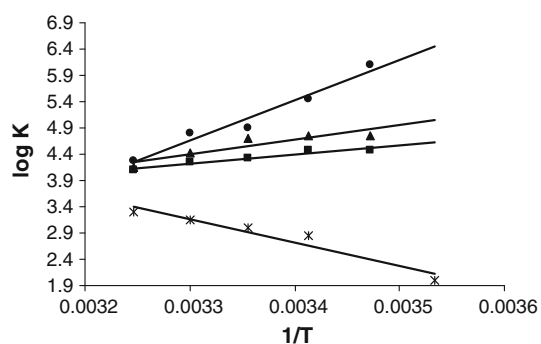


Fig. 2 Plot of $\log K$ versus $1/T$ for the compound **1** with Pb^{2+} (filled circles), Cu^{2+} (filled triangles), Zn^{2+} (filled squares) and Cd^{2+} (asterisk) in AN

Table 1 Thermodynamic parameters for **1** and **2** with Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} in AN at 298 K

Medium	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	Log K at 25 °C
1- Cu^{2+}	-48.9 ± 2.5	-79.2 ± 2.9	-25.3 ± 1.7	4.8
1- Pb^{2+}	-145.9 ± 7.3	-391.4 ± 19.6	-29.3 ± 1.4	5.0
1- Zn^{2+}	-33.5 ± 1.7	-29.7 ± 1.7	-24.7 ± 1.2	3.5
1- Cd^{2+}	85.3 ± 4.3	342.2 ± 17.4	-16.8 ± 0.8	3.0
2- Cu^{2+}	-6.3 ± 0.5	58.8 ± 1.4	-23.8 ± 1.1	4.2
2- Pb^{2+}	-120.9 ± 6.0	-307.4 ± 15.3	-29.2 ± 1.4	5.0

values are also negative except for **1**- Cd^{2+} and **2**- Cu^{2+} complexes which means that the complexation is entropic favored for these two complexes only. In agreement with most of the published work, this implies that the complex formation is exothermic process and the complex formation results a more ordered system. The formation of the complex results in a more ordered state of the system as the loosely bound solvent molecules are replaced by a positively charged species in the crown ether cavity. This accounts for loss of entropy accompanying complex formation. Results in Table 1 reveals a correlation between the values of ΔG° and ΔS° at 25 °C, the complex with higher value of ΔG° have higher ($-\Delta S^\circ$) value. This implies that the more stable complex formation is accompanied with a more ordered system, which is due to the stronger interaction between the crown and the metal ions.

Table 1 also shows that the complexes of Pb^{2+} with both **1** and **2** have the largest negative enthalpy changes, negative entropy changes and negative free energy changes. This observation is explained on the following bases: To accommodate a cation, the crown ether cavity seeks a certain conformation, such that the repulsion between any adjacent C–O or C–S dipoles is minimum and the interaction of these dipoles with the cation is maximum. The cation that best fulfills the requirements should have the large negative enthalpy and entropy changes. It seems that the size of Pb^{2+} ion as well as its softness allow it to be included in the cavity of each of **1** and **2** and has the strongest interaction with the C–S dipoles. For similar reason both Pb^{2+} and Cu^{2+} , which are considered soft cations, have stronger interaction with compound **1** which has five S atoms as compared to compound **2** which contains four S atoms. Complexes of Pb^{2+} with both ligands are the most stable, this result is in agreement with the HSAB theory. Ligands **2** and **1** have four and five sulfur atoms, which are softer than oxygen atoms and Pb^{2+} is also considered the softest cation among the cations used in this study [17].

Depending on the values of ΔG° , Table 1 clearly shows that ligand **1** form complexes with all cations and the stability sequence is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$, while ligand **2** was able to selectively bind only Pb^{2+} and Cu^{2+} with the following sequence; $\text{Pb}^{2+} > \text{Cu}^{2+}$. Similar trend was observed by Alpb et al. [18]. They synthesized new macrocyclic ligands containing nitrogen–sulfur donor atoms. They studied their extractability and selectivity toward some transition metal ions. Our ongoing research on this area is concentrating on preparing ligands that are selectively bind only one of these cations.

The complex of **1** with Cd^{2+} has the least stability among the other cations and also has a positive enthalpy change, but the complex formation is favored by entropic contribution. This is probably because a weaker interaction is associated with an entropy loss which is partially

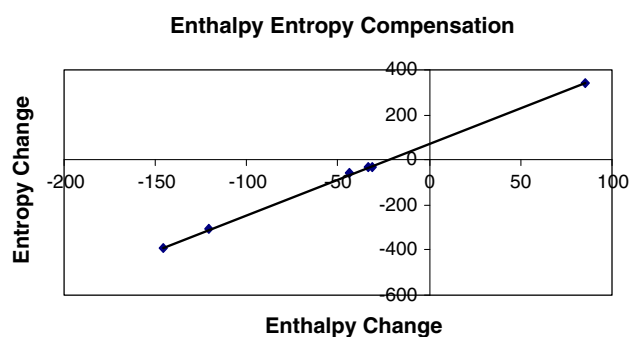


Fig. 3 Enthalpy entropy compensation for the complexation of **1** and **2** with metal cations studied

compensated by a simultaneous entropic gain due to greater degrees of freedom of the resulting complex.

The data in Table 1 shows that the values of $-\Delta H$ are correlated to the values of $-\Delta S$. Values of $-\Delta H$ increases as $-\Delta S$ values increases. This phenomena is known as “enthalpy–entropy compensation”. A plot of $T\Delta S^\circ$ against ΔH° (shown in Fig. 3) gave a straight line with a good correlation. The negative intercept ($T\Delta S^\circ$) value indicates that the complex formation is not favored in the absence of an enthalpic contribution. This emphasizes that the complex formation is entropy unfavored while it is enthalpy favored. Similar observation was noticed with other systems [19].

In conclusion, the results of this study revealed that, variation of the heteroatoms in the crown ether cavity altered the selectivity. Also it showed that the soft cation Pb^{2+} form the most stable complexes with our ligands.

Acknowledgment The authors thank Yarmouk University for financial support (project No. 24/2006).

References

1. Gunlaugsson, T., Leonard, J.P., Murray, N.S.: Highly selective colorimetric naked-eye Cu(II) detection using an azobenzene chemosensor. *Org. Lett.* **6**, 1557–1560 (2004)
2. Kim, J.Y., Kim, C.R., Lees, H., Lee, J.H., Ki, J.S.: UV band splitting of chromogenic azo-coupled calix[4]crown upon cation complexation. *J. Org. Chem.* **68**, 1933–1937 (2003)
3. Vetrichelvan, M., Lai, Y.-H., Mok, K.F.: 3,11,19-Tri-thia[3.3.3]pyridinophane: structural diversity in its transition metal complexes. *Eur. J. Inorg. Chem.* 2086–2095 (2004)
4. Contu, F., Dermartin, F., Devillanova, F.A., Garau, A., Isaia, F., Lippolis, V., Salis, A., Verani, G.: Conformationally locked mixed aza-thioether macrocycles: synthesis and structures of complexes of Pd^{II} , Pt^{II} and Rh^{III} of 2,5,8-trithia[9] (2,9)-1,10-phenanthrolinephane. *J. Chem. Soc., Dalton Trans.* 4401–4406 (1997)
5. Watzky, M.A., Wankine, D., Heeg, M.J., Endicott, J.F., Ochrymowycz, L.A.: Tetradentate macrocyclic complexes of platinum.

Evaluation of the stereochemical alterations of redox behavior and the x-ray crystal structure of (1,4,7,10-tetrathiacyclododecane) platinum(II) chloride. *Inorg. Chem.* **32**, 4882–4888 (1993)

6. Blake, A.J., Halcrow, M.A., Schröder, M.: Nickel thioether chemistry: syntheses of nickel(II) complexes of tetra- and penta-thia macrocyclic ligands. The single-crystal structures of $[Ni([16]aneS_4)(OH_2)_2][BF_4]_2$ and $[Ni([15]aneS_5)][PF_6]_2$ ($[16]aneS_4=1,5,9,13$ -tetrathia cyclohexadecane, $[15]aneS_5=1,4,7,10,13$ -pentathiacyclopentadecane). *J. Chem. Soc., Dalton Trans.* 2803–2808 (1992)
7. Lee, S.J., Jung, J.H., Seo, J., Yoon, I., Park, K.-M., Lindoy, L.F., Lee, S.S.: A chromogenic macrocycle exhibiting cation-selective and anion-controlled color change: an approach to understanding structure–color relationships. *Org. Lett.* **8**, 1641–1643 (2006)
8. Seo, J., Song, M.R., Lee, J.-E., Lee, S.Y., Yoon, I., Park, K.-M., Kim, J., Jung, J.H., Park, S.B., Lee, S.S.: Exo-coordination-based supramolecular silver(I) complexes of S_2O macrocycles: effect of ligand isomerism on the structural diversity. *Inorg. Chem.* **45**, 952–954 (2006)
9. Yoon, I., Seo, J., Park, K.-M., Kim, J.S., Lah, M.S., Lee, S.S.: Assembly of a heterobinuclear 2-D network: a rare example of endo- and exocyclic coordination of Pd^{II}/Ag^I in a single macrocycle. *Inorg. Chem.* **45**, 3487–3489 (2006)
10. Yoon, I., Seo, J., Lee, J.-E., Song, M.R., Lee, S.Y., Choi, K.S., Jung, O.-S., Park, K.-M., Lee, S.S.: Donor effect on supramolecular structures of silver(I) perchlorate complexes of macrocycles with O_2S_2X ($X = S, O$ and NH) donor sets. *J. Chem. Soc., Dalton Trans.* 2352–2354 (2005)
11. Kim, H.J., Yoon, I., Lee, S.Y., Seo, J., Lee, S.S.: A flexible dibenzo- O_4S_2 -macrocyclic: *twist-and-squeeze* type metal binding via synergic action of metal–ligand and metal– π interaction. *Tetrahedron Lett.* **48**, 8464–8467 (2007)
12. Dmitrieva, S.N., Sidorenko, N.I., Kuz'mina, L.G., Buslaeva, T.M., Basok, S.S., Buryak, A.K., Howard, J.A.K., Gromov, S.P.: Synthesis and crystal structure of *cis* and *trans* complexes of benzodithia-18(21)-crown-6(7) ethers with $PdCl_2$. *Mendeleev Commun.* **19**, 21–23 (2009)
13. Ashram, M.: A convenient synthesis of novel 20-, 23-, and 26-membered macrocyclic oxathiadibenzo- and oxathiadinaphthalenocrown ethers, Part 1. *Z. Naturforsch* **60b**, 891–900 (2005)
14. Mizyed, S.A.: Thermodynamic study of the association of alkali metal cations with some crown ethers. M. Sc. Dissertation, Yarmouk University, Jordan (1987)
15. Tawarah, K.M., Mizyed, S.A.: A conductance study of the binding of benzo-15-crown-5 with alkali cations in acetonitrile. *J. Incl. Phenom. Macrocycl. Chem.* **6**, 583–591 (1988)
16. Pourghobadi, Z., Majidi, F., Asli, M., Parasa, F., Moghimi, M., Ganjali, M., Aghabozorg, H., Shamsipur, M.: Synthesis of a new triazine derived macrocycle and a thermodynamic study of its complexes with some transition and heavy metal ions in acetonitrile solution. *Pol. J. Chem.* **74**, 837–846 (2000)
17. Pearson, R.G.: Hard and soft acids and bases. *J. Am. Chem. Soc.* **85**(22), 3533–3539 (1963)
18. Alpb, H., Kantekina, H., Ocaka, U.: Synthesis and metal ion binding properties of thiaaza crown macrocycles. *J. Hazard. Mater* **159**, 519–522 (2008)
19. Mizyed, S., Ashram, M., Saymeh, R., Marji, D.: A thermodynamic study of the charge transfer complexes of iodine with different *tert*-butylcalix[4]crowns. *Z. Naturforsch* **60**, 1133–1137 (2005)