Polish J. Chem., **78**, 109–116 (2004) **PHYSICAL CHEMISTRY**

Conductance Study of the Thermodynamics of Dibenzopyridino-18-crown-6 Complexes with K^+, Tl^+, Sr^{2+} and Ba^{2+} Ions in Acetonitrile Solution

by M. Shamsipur[1]* and N. Tavakkoli[2]

[1]*Department of Chemistry, Razi University, Kermanshah, Iran*
[2]*Department of Chemistry, Shiraz University, Shiraz, Iran*

(Received June 11th, 2003)

The complexation reactions between dibenzopyridino-18-crown-6 and Tl^+, K^+, Sr^{2+} and Ba^{2+} ions were studied conductometrically in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. At 25°C, the stability of the resulting complexes varied in the order $Ba^{2+} > Sr^{2+} > Tl^+ > K^+$. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. While, the bivalent alkaline earth complexes are both enthalpy and entropy stabilized, the univalent cation complexes used are enthalpy stabilized but entropy destabilized.

Key words: dibenzopyridino-18-crown-6, K^+, Tl^+, Sr^{2+} and Ba^{2+} complexes, stability, enthalpy, entropy, acetonitrile, conductance

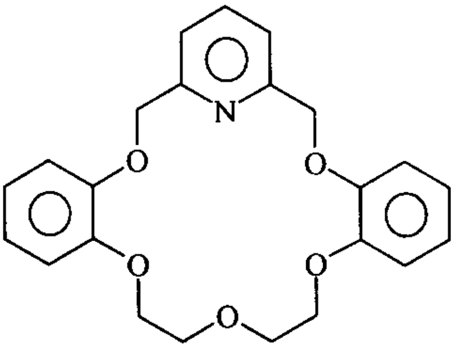
Macrocyclic ligands have demonstrated potential for use in many industrial and chemical processes, where cation selectivity and/or solubility in nonpolar solvents are required [1,2]. For this reason, the synthesis of simple and inexpensive macrocycles with various cation selectivities is desirable. In recent years, considerable effort has been devoted to the design of new synthetic macrocyclic ligands. The stability and selectivity of metal ion complexes with these ligands are matched with those of the naturally occurring antibiotics such as valinomycin [3,4]. Meanwhile, due to the importance of the selectivity and stability of the macrocyclic complexes with different cations in a wide variety of practical applications [5–7], extensive amount of work on the thermodynamic aspects of the corresponding complexation reactions has been carried out [8–10].

In addition, donor atoms such as sulfur, amine nitrogen, and pyridine nitrogen have been used to replace the oxygen atoms in crown ether rings in order to vary the cation binding characteristics of these ligands [11,12]. The evaluation of pyridine nitrogen as a macrocyclic donor atom is also desirable. Cram and co-workers have shown that pyridino-18-crown-6, which incorporates a pyridine subcyclic unit, in its macrocyclic frame, forms complexes with alkylammonium cations, which are more stable thermodynamically than those formed with 18-crown-6 [13,14].

---

* Author for correspondence.

In this paper we report a conductance study of the thermodynamics of complexation of K^+, Tl^+, Sr^{2+} and Ba^{2+} ions with dibenzopyridino-crown-6 in acetonitrile solution. We have recently reported the thermodynamics of complexation of some transition and heavy metal ions with dibenzopyridino-18-crown-6, (DBPYl8C6) in methanol solution by a competitive potentiometric method [15].



DBPY18C6

EXPERIMENTAL

Reagent grade potassium nitrate (Fluka), thallium perchlorate (K & K), barium perchlorate (Fluka) and DBPYl8C6 (Merck) were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Strontium perchlorate was prepared from the reaction of $SrCO_3$ and $HClO_4$ (both from Merck). The resulting strontium perchlorate salt was recrystallized several times from deionized water and dried in vacuum oven at about 150°C for 48 h. Finally, the salt was further dried at 200–250°C under a flow of nitrogen for 24 h. Reagent grade acetonitrile (Merck) was used as received.

Conductance measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell, made platinum black, was used. The cell constants at various temperatures used was determined by measuring the conductivity of a 0.010 M solution of analytical grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures have been reported in the literature [16]. In all experiments, the cell was thermostated at the desired temperature ±0.03°C using a Lo-Temprol 154 Precision Scientific thermostat.

In a typical experiments,15 ml of the desired metal ion (3.3×10^{-5}–7.7×10^{-5} M) was placed in the titration cells thermostated to the desired temperature and the conductance of the solution was measured. Then, a known amount of the crown ether solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand solution was continued until the desired ligand to cation mole ratio was achieved.

The formation constants, K_f, and the limiting molar conductances, Λ_{obs}, of the resulting 1:1 complexes between DBPY18C6 and different cations in acetonitrile at various temperatures were calculated by fitting of the observed molar conductances, Λ_{obs}, at various macrocycle/cation mole ratios to the previous derived equations [17,18], which express the Λ_{obs} as a function of the free and complexed metal ions and the formation constant by using a nonlinear least-squares program KINFIT [19]. The details are described elsewhere [20–23].

RESULTS AND DISCUSSION

In order to evaluate the effect of adding crown ethers on the molar conductance of K^+, Tl^+, Sr^{2+} and Ba^{2+} cations in acetonitrile solutions, the conductivity at a constant salt concentration (3.3×10^{-5}–7.7×10^{-5} M) was monitored while increasing the crown ether concentration at various temperatures. The resulting molar conductance *vs.* DBPY18C6/cation mole ratio at various temperatures are shown in Figures 1–4.

From Figures 1–4 it is obvious that, in all cases studied, addition of the crown ethers to the metal ion solutions causes a rather large and continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the complexed cations compared to the free ones. As can be seen from Figures 1–4, in the case of Ba^{2+} at all temperatures and in the case of other cations at lower temperatures, the slope of the corresponding molar conductance-mole ratio plots changes sharply at the point, where the ligand to cation mole ratio is one and further addition of the ligand causes no significant change in the molar conductance. Such a conductance behavior is indicative of the formation of fairly stable 1:1 complexes in solution. While, in other cases, although the molar conductance does not show any tendency to level off even at the molar ratios > 2, the corresponding mole ratio data show a considerable change in their slopes at a mole ratio of about one, emphasizing the formation of some weaker 1:1 complexes.

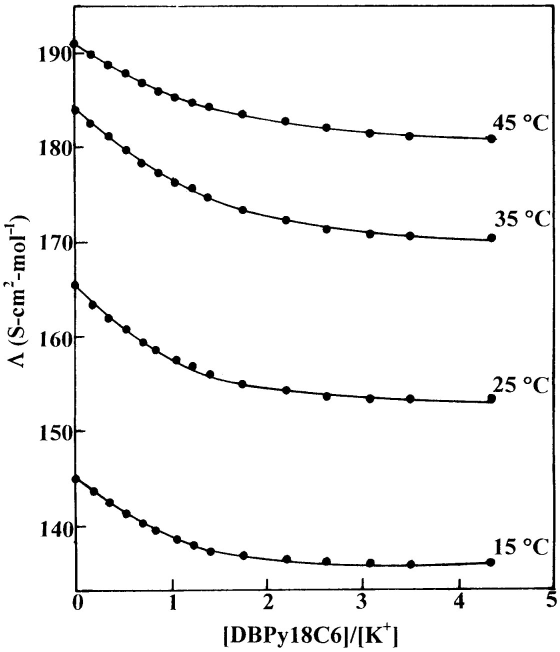


Figure 1. Molar conductance *vs.* $[K^+]$/[DBPy18C6] plots in acetonitrile at various temperatures.

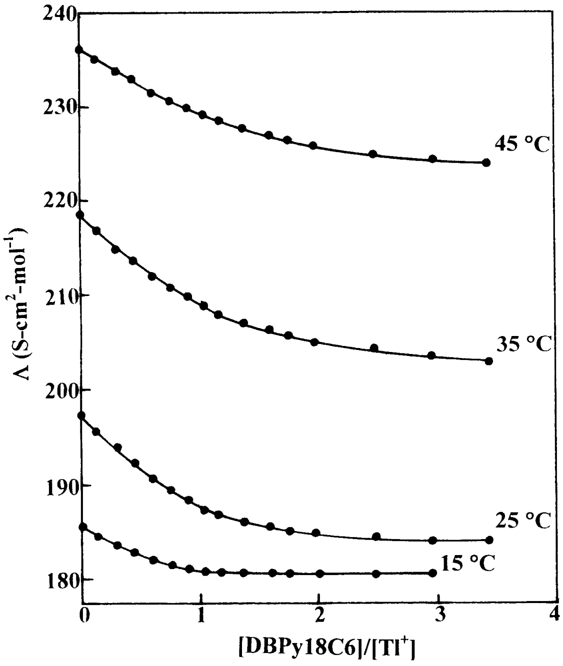


Figure 2. Molar conductance *vs*. [Tl^+]/[DBPy18C6] plots in acetonitrile at various temperatures.

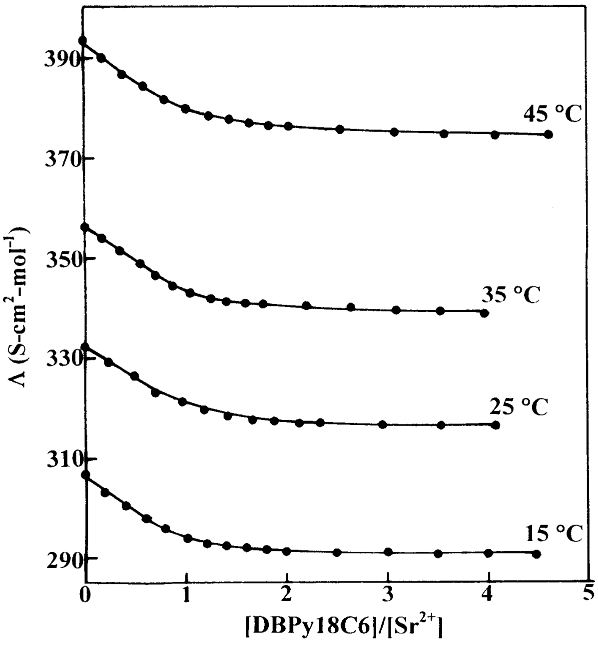


Figure 3. Molar conductance *vs*. [Sr^{2+}]/[DBPy18C6] plots in acetonitrile at various temperatures.

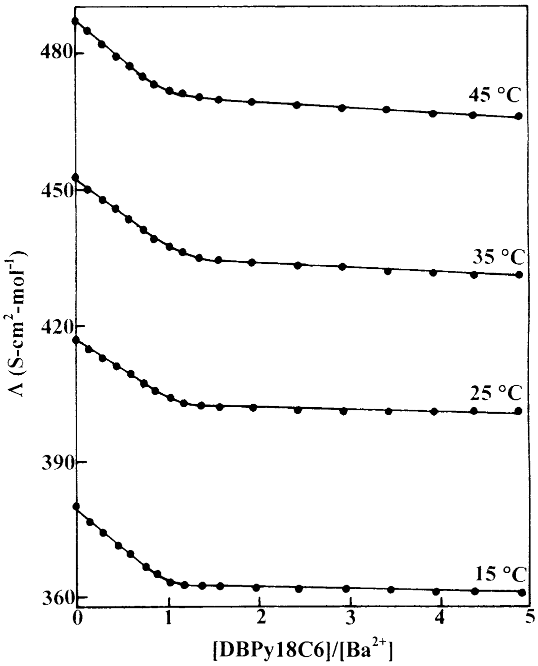


Figure 4. Molar conductance *vs*. $[Ba^{2+}]/[DBPy18C6]$ plots in acetonitrile at various temperatures.

In order to have a better understanding of the thermodynamics of the complexation reactions of K^+, Tl^+, Sr^{2+} and Ba^{2+} ions with DBPY18C6, it is useful to consider the enthalpic and entropic contributions to these reactions. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ of the complexation reactions of the metal ions used with DBPY18C6 were evaluated by measuring the formation constants as a function of temperature. The formation constants of all DBPY18C6-M^{n+} complexes in acetonitrile at various temperatures, obtained by computer fitting of molar conductance-mole ratio data, are listed in Table 1. A sample computer fit of mole ratio data is shown in Figure 5. Our assumption of 1:1 stoichiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductances. It should be noted that, in the procedure of calculation of formation constants, the association between M^{n+} and the bulky ClO_4^- or NO_3^- anions was considered negligible, under the highly dilute experimental conditions used. Furthermore, since the concentration of crown ethers was kept below 1.0×10^{-3} M during the conductometric titrations, the corrections for viscosity changes were also neglected.

Vant Hoff plots of log K_f *vs.* 1/T for different DBPY18C6-M^{n+} complexes were linear for all cases studied, as shown in Figure 6. The enthalpies and the entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are also included in Table 1.

Table l. Formation constants and enthalpy and entropy changes for different M^{n+}-DBPy18C6 complexes in acetonitrile solution.

Cation[a]	log K_f				ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
	15°C	25°C	35°C	45°C		
Tl^+ (1.49)	5.68±0.05	5.18±0.05	4.90±0.03	4.48±0.04	–70± 6	–135±6
K^+ (1.38)	4.70±0.03	4.52±0.04	4.29±0.05	4.18±0.02	–31± 2	–19±6
Sr^{2+} (1.18)	5.38±0.04	5.28±0.03	5.21±0.05	5.03±0.04	–20± 3	35±10
Ba^{2+} (1.35)	5.73±0.04	5.51±0.03	5.29±0.04	5.13±0.05	–30± 1	131±4

[a] Cationic radii in Å are given in parentheses.

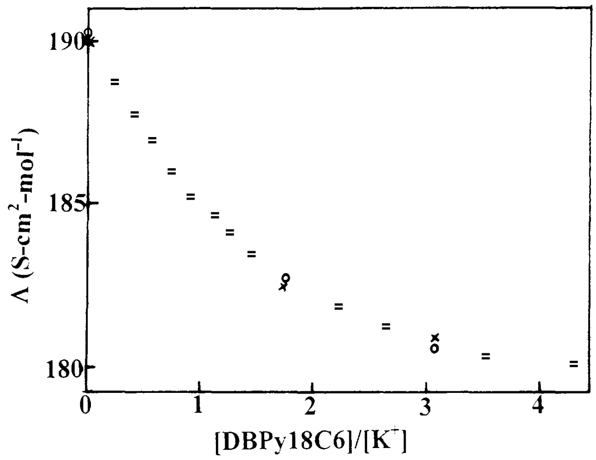


Figure 5. Computer fit of the molar conductance-mole ratio data for K^+-DBPy18C6 at 45°C in acetonitrile: (x) experimental point: (o) calculated point: (=) experimental and calculated points are the same within the resolution of the plot.

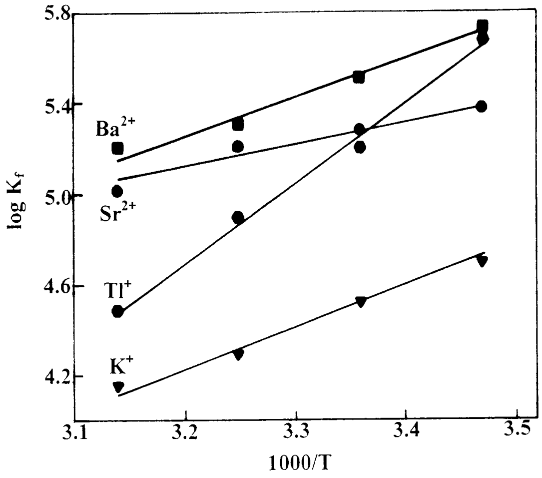


Figure 6. Van't Hoff plots for K^+, Tl^+, Sr^{2+} and Ba^{2+} complexes with DBPy18C6 in acetonitrile solution.

The data given in Table 1 revealed that, at 25°C, the stability of the 1:1 complexes of DBPY18C6 with different cations decrease in the order $Ba^{2+} > Sr^{2+} > Tl^{+} > K^{+}$. While , the ionic sizes of Ba^{2+} (2.70 Å) and K^{+} (2.76 Å) [24] are convenient for fitting inside the cavity of DBPY18C6 (2.68–2.86 Å) [25], the size of Sr^{2+} ion (2.36 Å) is too small for the macrocycle's cavity. Despite this fact, the Sr^{2+} ion was observed to form a more stable DBPY18C6 complex than do the univalent Tl^{+} and K^{+} ions. This is most probably due to the increased charge density of bivalent Sr^{2+} ion, which results in much stronger interaction with donating atoms of the macrocycle.

On the other hand, the monovalent thallium ion is a polarizable soft ion [26], which has been suggested as a probe for potassium ion in biological systems [27,28]. It can substitute for K^{+} in activation of some important enzymes such as ATPase [29] and pyruvate [30]. Thus, information about the stability and selectivity of Tl^{+} complexes with macrocyclic ligands are of special interest in this respect. It has been frequently reported that Tl^{+} ion forms somewhat less stable complexes than K^{+} ion with ordinary crown ethers such as 18-crown-6 and dicyclohexyl-18-crown-6. While, in this work, the Tl^{+} complex with DBPY18C6 revealed a large increase in stability over the K^{+}-DBPY18C6 complex. The observed increased stability of the Tl^{+} complex could be due to the stronger interaction of the pyridine nitrogen of the ligand as a soft base with Tl^{+} as a soft acid, in comparison with the hard K^{+} ion [26].

As is obvious from Table 1, despite its hard character, Ba^{2+} ion forms the most stable complex with DBPY18C6 in the series. This is not only because of the proper fitting condition of the cation for the macrocycle's cavity, but also because of its increased charge density, over the univalent K^{+} and Tl^{+} ions.

REFERENCES

1. Schwind R.M., Gilligan T.J. and Cussler E.L., Synthetic Multidentate Macrocyclic Compounds, Academic Press, NY (1978).
2. Cooper S.R. (ed.), Crown Compounds; Toward Future Applications, VCH Publishers, NY (1992).
3. Bradshaw J.S. and Stott P.E., *Tetrahedron*, **36**, 461 (1980).
4. Hancock R.D. and Martell A.E., *Chem. Rev.*, **89**, 1875 (1989).
5. Izatt R.M., Clark G.A., Bradshaw J.S., Lamb J.D. and Christensen J.J., *Sep. Purif. Methods*, **15**, 21 (1986).
6. Shih J.-S., *J. Chin. Chem. Soc.*, **39**, 551 (1992).
7. Bühlmann P., Pretsch E. and Bakker E., *Chem. Rev.*, **98**, 1593 (1998).
8. Izatt R.M., Bradshaw J.S., Nielsen S.A., Lamb J.D., Christensen J.J. and Sen D., *Chem. Rev.*, **85**, 271 (1985).
9. Izatt R.M., Pawlak K., Bradshaw J.S. and Bruening R.L., *Chem. Rev.*, **91**, 1721 (1991).
10. Izatt R.M., Pawlak K., Bradshaw J.S. and Bruening R.L., *Chem. Rev.*, **95**, 2529 (1995).
11. Frensdorff H.K., *J. Am. Chem. Soc.*, **93**, 600 (1971).
12. Fore P.E., Bradshaw J.S. and Nielsen S.F., *J. Heterocycl. Chem.*, **15**, 269 (1978).
13. Cram D.J. and Cram J.M., *Science*, **183**, 803 (1974).
14. Newcomb M., Timko J.M. and Cram D.J., *J. Am. Chem. Soc.*, **99**, 6392 (1977).
15. Shamsipur M. and Zolgharnein J., *J. Incl. Phenom.*, **40**, 41 (2001).
16. Wu Y.C. and Koch W.F., *J. Solution Chem.*, **20**, 391 (1991).
17. Yakeda Y., *Bull. Chem. Soc. Jpn.*, **56**, 3600 (1983).

18. Zollinger D.P., Bulten F., Christenhuse A., Bos M. and van der Linden W.E., *Anal. Chim. Acta*, **198**, 207 (1987).
19. Nicely V.A. and Dye J.L., *J. Chem. Educ.*, **48**, 443 (1971).
20. Amini M.K. and Shamsipur M., *Inorg. Chim. Acta*, **183**, 65 (1991).
21. Hassani M. and Shamsipur M., *J. Solution Chem.*, **23**, 721 (1994).
22. Ganjali M.R., Rouhollahi A., Mardan A.R. and Shamsipur M., *J. Chem. Soc., Farad. Trans.*, **94**, 1959 (1998).
23. Shamsipur M. and Saeidi M., *J. Solution Chem.*, **29**, 1187 (2000).
24. Shannon R.D., *Acta Cryst.*, **32A**, 751 (1976).
25. Pedersen C.J., *J. Am. Chem. Soc.*, **92**, 386 (1970).
26. Pearson R.G., *J. Am. Chem. Soc.*, **85**, 3233 (1963).
27. Kayne F.J. and Ruben J., *J. Am. Chem. Soc.*, **92**, 220 (1970).
28. Williams R.J.F., *Quart. Rev. Chem. Soc.*, **24**, 331 (1970).
29. Britten J.S. and Blank M., *Biochim. Biophys. Acta*, **159**, 160 (1968).
30. Kayne F.J., *Arch. Biochem. Biophys.*, **143**, 232 (1971).