



Competitive Potentiometric Study of the Thermodynamics of Complexation of Some Transition and Heavy Metal Ions with Dibenzopyridino-18-crown-6 in Methanol Using Ag^+ Ion as a Probe

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(Received: 22 June 2000; in final form: 1 December 2000)

Key words: competitive potentiometry, dibenzopyridino-18-crown-6 complexes, thermodynamics.

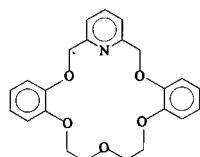
Abstract

The complexation of dibenzopyridino-18-crown-6 with some transition and heavy metal ions in methanol solution at various temperatures was studied by a competitive potentiometric method using a Ag^+/Ag electrode system. The stoichiometry and stability of the resulting complexes were computed by the MINIQUAD program. The stability of the resulting complexes varied in the order $\text{Ag}^+ > \text{Pb}^{2+} > \text{Tl}^+ > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The enthalpy and entropy of the resulting 1 : 1 complexes were evaluated from the temperature dependence of the stability constants. The complexes of all cations were enthalpy-stabilized but entropy-destabilized, except for Ag^+ and Pb^{2+} ions, which were also entropy-stabilized.

Introduction

The ability of crown ethers [1] to selectively bind cations [2–4] stimulated the design of new cyclic polyethers that as host compounds can form highly structured molecular complexes with appropriate guest compounds [5–7]. The feasibility of introducing into host molecules pyridyl units, which can act as binding and shaping sites for specific guest compounds was first reported by Newcomb *et al.* [8]. It has been clearly shown that 2,6-pyridinedimethyl units can be substituted for $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ units in the design and synthesis of host molecules for forming highly structured molecular complexes [9–11].

In recent years, we have been involved in spectroscopic and electrochemical studies of the thermodynamics and kinetics of macrocyclic ligand-metal ion binding in non-aqueous and mixed solvents [12–16]. We have also used dibenzopyridino-18-crown-6 (DBPY18C6, **I**) for charge-transfer complexation with iodine [11] and, as a suitable neutral ion carrier, in construction of a new Pb^{2+} ion-selective electrode [17]. In this paper we report the thermodynamic study of complexation of DBPY18C6 with Ag^+ , Tl^+ , Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} ions in methanol solution by a competitive potentiometric method using Ag^+ ion as a suitable auxiliary ion.



I

Experimental

Reagent grade DBPY18C6 and nitrate salts of silver, thallium, lead, cadmium, zinc and copper (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Absolute methanol (Merck) was used as solvent. Tetrabutylammonium perchlorate (TBAP) was prepared from the 1 : 1 interaction of reagent grade perchloric acid and tetrabutylammonium bromide (both from Merck). The resulting TBAP salt was recrystallized three times from triply distilled deionized water and dried at 110°C for 72 h.

A Ag^+/Ag concentration cell was used to monitor the concentration of silver ion during the potentiometric titration of Ag^+ ion with a solution of the crown in the presence and absence of other metal ions used [18]. The concentration of free silver ion was measured with a silver electrode, potentials being measured with a digital voltmeter (model 624 Metrohm). The reference electrode was a Ag^+/Ag electrode, immersed in a known solution of AgNO_3 (2.51×10^{-4} M) in methanol and separated from the test solution by a salt bridge containing 0.1 M TBAP in the same solvent. In all experiments, the cell was thermostated at the desired temperature $\pm 0.05^\circ\text{C}$, using a Huber thermostat.

To evaluate the stability constants, the following procedure was conducted. The silver electrode was placed in the reaction vessel containing 20 mL of 0.5 M TBAP in methanol. The reference compartment contained 0.05 M TBAP and 2.51×10^{-4} M silver nitrate in the same solvent. First, a concentrated silver nitrate solution (0.013 M) was added gradually until a Ag^+ ion concentration of 2.51×10^{-4} M was achieved, and the cell potential was measured. At various temperatures, the plots of emf vs $\log [\text{Ag}^+]$ were strictly linear (with regression coefficients > 0.994), possess-

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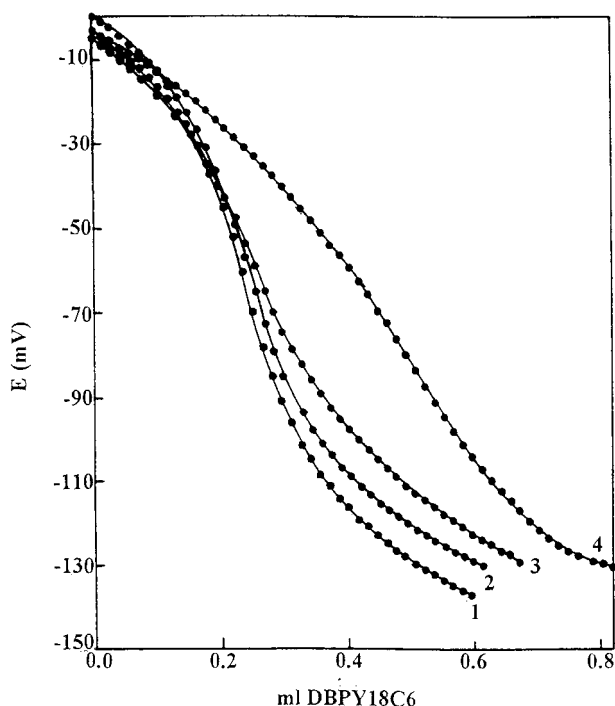


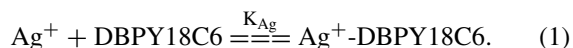
Figure 1. Sample potentiometric titration curves of a 2.51×10^{-4} M AgNO_3 with DBPY18C6 (0.023 M) in the absence (1) and presence of equimolar concentrations of other metal ions in methanol at 25°C and ionic strength of 0.5 M TBAP: (2) Cu^{2+} ; (3) Tl^+ ; (4) Pb^{2+} .

ing a near-Nernstian slope. The same solution was then back titrated with a concentrated DBPY18C6 solution (0.023 M), in the presence and absence of other metal ions M^{n+} , in the same solvent (Figure 1).

All titrations were carried out using a Metler electronic burette with a precision of ± 0.001 mL. In all experiments, the ionic strength was kept constant at $I = 0.05$ M using TBAP as supporting electrolyte.

Results and discussion

The stability constant of the Ag^+ -DBPY18C6 complex (Equation 1) at various temperatures, K_{Ag} , can be determined by simple potentiometric titration of Ag^+ ion with a solution of the ligand.



For a solution containing Ag^+ and DBPY18C6, the total concentrations can be written as

$$[\text{Ag}^+]_{\text{tot}} = [\text{Ag}^+] + [\text{Ag}^+\text{-DBPY18C6}], \quad (2)$$

$$[\text{DBPY18C6}]_{\text{tot}} = [\text{DBPY18C6}] + [\text{Ag}^+\text{-DBPY18C6}]. \quad (3)$$

The stability constants of the M^{n+} ion complexes, K_{M} , with DBPY18C6 (Equation 4) at various temperatures can be determined by the double decomposition reaction of M^{n+}

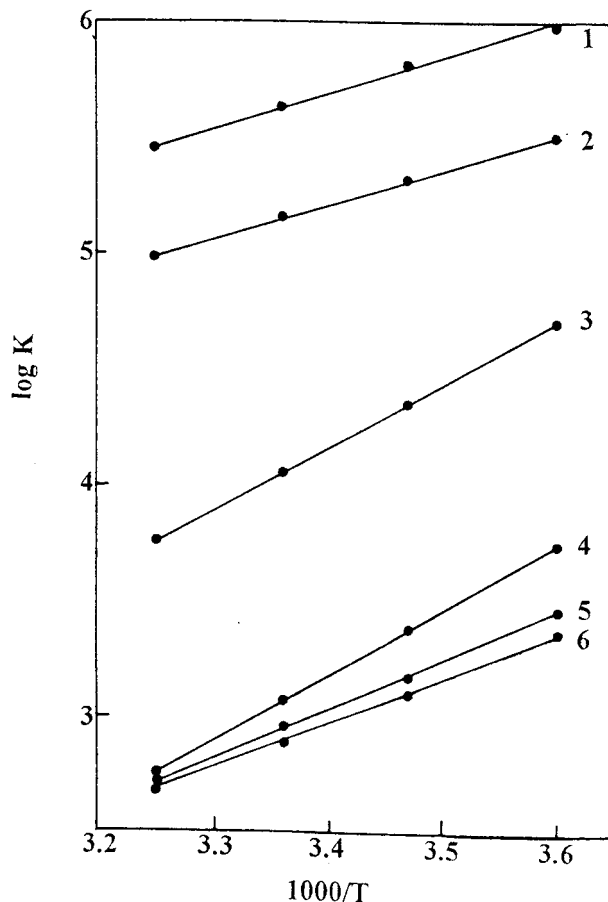
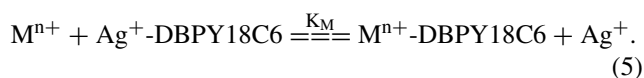
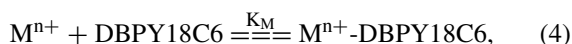


Figure 2. Van't Hoff plots for DBPY18C6 complexes with different metal ions in methanol solution: (1) Ag^+ ; (2) Pb^{2+} ; (3) Tl^+ ; (4) Cu^{2+} ; (5) Zn^{2+} ; (6) Cd^{2+} .

with the corresponding Ag^+ complex (Equation 5) by monitoring the equilibrium concentration of silver ion in the presence of M^{n+} ions using the equilibrium constant $K_{\text{E}} = K_{\text{M}}/K_{\text{Ag}}$ for reaction 5 together with the stability constant K_{Ag} obtained from direct titration of Ag^+ ion with the ligand.



In this case, the total concentrations of M^{n+} and DBPY18C6 is written as

$$[\text{M}^{n+}]_{\text{tot}} = [\text{M}^{n+}] + [\text{M}^{n+}\text{-DBPY18C6}], \quad (6)$$

$$[\text{DBPY18C6}]_{\text{tot}} = [\text{DBPY18C6}] + [\text{Ag}^+\text{-DBPY18C6}] + [\text{M}^{n+}\text{-DBPY18C6}]. \quad (7)$$

A MINIQUAD program was used to compute the formation constants K_{Ag} and K_{M} from the resulting potential-concentration data [19, 20]. By using the Gauss-Newton least-squares method, MINIQUAD refines the formation

Table 1. Thermodynamic parameters for complexation of DBPY18C6 with different transition and heavy metal ions in methanol at various temperatures^a

Cations	$\log K \pm \sigma$				ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
	5 °C	15 °C	25 °C	35 °C		
Pb ²⁺	5.48 ± 0.03	5.29 ± 0.04	5.14 ± 0.05	4.97 ± 0.03	-27.6 ± 0.5	6 ± 2
Ag ⁺	5.98 ± 0.01	5.79 ± 0.01	5.63 ± 0.01	5.45 ± 0.01	-28.7 ± 0.5	11 ± 2
Tl ⁺	4.69 ± 0.05	4.36 ± 0.01	4.04 ± 0.01	3.74 ± 0.01	-52.0 ± 0.3	-97 ± 1
Cu ²⁺	3.70 ± 0.09	3.38 ± 0.06	3.05 ± 0.04	2.75 ± 0.10	-52.2 ± 0.5	-117 ± 2
Zn ²⁺	3.44 ± 0.10	3.14 ± 0.10	2.98 ± 0.10	2.70 ± 0.10	-46.1 ± 0.3	-100 ± 1
Cd ²⁺	3.36 ± 0.10	3.10 ± 0.10	2.85 ± 0.10	2.66 ± 0.10	-38.1 ± 0.3	-73 ± 2

^a The sum of square of residuals, X² and R values associated with the formation constants were in the range of 0.4 ± 10^{-8} – 2.30×10^{-8} , 2.2–56.7 and 0.01–0.04, respectively.

constants of the simultaneous complexation equilibria. Using the initial estimates of the formation constants, the set of simultaneous normal equations is built up and then solved in order to obtain the corrections to be applied to the K values. The new values of the formation constants are a better approximation to the final values and, consequently, are employed in the next refinement cycle. Such an iterative procedure provides K values which result in the best agreement between calculated and experimental data. The acceptance of final results at the desired significance levels is based upon such statistical parameters as the standard deviation, the sum of square of residuals, the X² value as a measure of the normality of residuals and the R factor.

To obtain a better understanding of the thermodynamics of the complexation reactions, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy changes were determined by measuring the stability constants as a function of temperature. Thus, the procedure for the evaluation of the formation constants was followed at four different temperatures and all calculated values are summarized in Table 1. Plots of $\log K$ vs $1/T$ for all DBPY18C6 complexes studied were rectilinear (Figure 2). The changes in enthalpy and entropy of complexation were determined in the usual manner from the slopes and intercepts of the resulting van't Hoff plots, respectively, and the results are also included in Table 1.

From the data given in Table 1, it is immediately obvious that the stability of the resulting complexes vary in the order $\text{Ag}^+ > \text{Pb}^{2+} > \text{Tl}^+ > \text{Cu}^{2+} > \text{Cd}^{2+} \sim \text{Zn}^{2+}$. The ionic size of Cu²⁺ (1.54 Å), Zn²⁺ (1.48 Å) and Cd²⁺ (1.90 Å) ions [21] are too small for the cavity of DBPY18C6 (2.68–2.86) [22] and, thus, it is not surprising to observe the smallest stability for their complexes in the series. The increased stability of the Cu²⁺ complex over that of the Zn²⁺ complex follows the Irving–Williams order [23] which generally holds for the equilibrium constants of first series transition metals [16].

On the other hand, among Ag⁺ (2.30 Å), Tl⁺ (3.00 Å) and Pb²⁺ (2.38 Å) cations, the size of the Tl⁺ ion seems to be a little larger than the cavity of DBPY18C6 so that it forms a weaker complex with the ligand than the two other cations studied. While, Pb²⁺ and Ag⁺ ions with the most suitable size for the crown ether's cavity form the most stable DBPY18C6 complexes among all the cations studied. It is interesting to note that the bivalent Pb²⁺ ion of about

the same ionic size as the univalent Ag⁺ ion is expected to form a more stable complex with DBPY18C6, due to its increased electrostatic interaction with the donating groups of the macrocyclic ring. The reverse situation is actually observed: Ag⁺-DBPY18C6 is more stable than the Pb²⁺-DBPY18C6 complex. Such an unexpected stability of the Ag⁺ complex could be partly due to the stronger interaction of the pyridino nitrogen of the ligand as a soft base with the Ag⁺ ion as a much softer acid than the Pb²⁺ ion [24]. Moreover, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, an understanding from the 'ion-in-the-hole' model [2], but a measure of the relative strength as compared to the ionic solvation. Thus, it is only for the weakly solvated larger univalent ions such as Ag⁺ and Tl⁺ that the cation size can be considered primarily responsible for the complexing characteristics. While, in the case of bivalent cations such as Pb²⁺ and, especially, smaller metal ions of the first transition series, the cation is so strongly solvated that considerably more energy must be expended in the desolvation step than for univalent cations. Contributions of the solvent-complex and even solvent-ligand interactions on the stability of the resulting complexes cannot be ignored.

From the data given in Table 1, it is readily seen that all DBPY18C6 complexes are enthalpy-stabilized. But, with the exception of the Ag⁺ and Pb²⁺ complexes, all other complexes are entropy-destabilized. However, the Ag⁺ and Pb²⁺ complexes are also entropy-stabilized. In the latter cases, where the Ag⁺ and Pb²⁺ ions can conveniently fit inside the cavity of the crown ether, and are properly isolated from the solvent molecules, the desolvation of the cations in the process of complex formation seems to have a dominant role in the resulting positive ΔS^0 values of the corresponding complexes. However, in the case of cations with either larger or smaller ionic sizes than the cavity of DBPY18C6, the complexed cations will still remain exposed to the solvent molecules so that the solvation of the cation complex may have a negative contribution to the ΔS^0 values of the cation-macrocyclic systems. Moreover, the decrease in conformational entropy of the crown ether, brought about upon complex formation with the metal ions [25], may result in decreased entropy of the systems studied. Thus, a balance between the above mentioned positive and negative contributions to entropy changes will result in the observed negative ΔS^0 values.

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