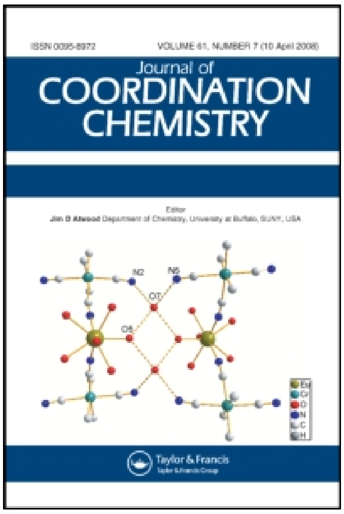

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SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF ALKALINE EARTH CRYPTATES IN DIMETHYLSULFOXIDE

Jahanbakhsh Ghasemi[a]; Mojtaba Shamsipur[a]
[a] Department of Chemistry, Shiraz University, Shiraz, Iran

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SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF ALKALINE EARTH CRYPTATES IN DIMETHYLSULFOXIDE

JAHANBAKHSH GHASEMI and MOJTABA SHAMSIPUR*

Department of Chemistry, Shiraz University, Shiraz, Iran

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Complexation of Ca^{2+}, Sr^{2+} and Ba^{2+} with cryptands C222, C221, C211 and C22 have been studied in dimethylsulfoxide solution by means of a competitive spectrophotometric technique using murexide as a metal ion indicator. Stabilities of the resulting 1:1 complexes were investigated at different temperatures and enthalpies and entropies of complexation were determined from the temperature dependence of the formation constants. In most cases, a pronounced "cryptate effect" was observed for bicyclic cryptates over corresponding monocyclic complexes; this was characterized by high selectivity and stability. The increased stability is caused by favourable entropic contributions.

KEYWORDS: Alkaline earth, cryptate, DMSO, stability, thermodynamics, spectrophotometry.

INTRODUCTION

It is well known that some of the alkali and alkaline earth cations are widely distributed in living organisms. These cations play fundamental roles in a wide variety of biological activities (*e.g.*, transmission of nerve impulses, muscle contraction, *etc.*), many of which are based on selective complexation and transport of a given cation.[1,2] Cryptand molecules, as synthesized by Lehn and coworkers,[3] are in many respects similar to naturally occurring molecules such as the ionophoric antibiotics[4] and, therefore, are among lignads that can be used as models for studying such cation selectivities.[5,6] Stability constants and thermodynamic data for the reaction of alkali ions with cryptands in aqueous and non-aqueous solutions have been reported.[7,8] On the other hand, few data are available for the alkaline earth cryptates, especially in non-aqueous media.

We have been involved in a study of the thermodynamics[9-11] and kinetics[12-14] of alkali and alkaline earth complexes with different macrocyclic ligands in non-aqueous solutions. In this paper we report a thermodynamic study of Ca^{2+}, Sr^{2+} and Ba^{2+} complexes with cryptands C222, C221, C211 and C22 (Fig. 1) in dimethylsulfoxide, as a solvent of relatively high dielectric constant ($\varepsilon = 46.7$) and

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* Author for correspondence.

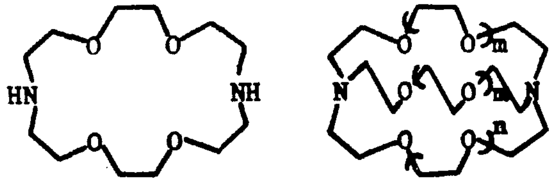

Figure 1 Structures of ligands; C22 is shown on the left. On the right, C211 has m = 0, n = 1, C221 has m = 1 and n = 0 and C222 has m = n = 1.

high donor number (DN = 29.8),[15] by a previously described visible spectroscopic technique using murexide as a metal ion indicator.[16,17]

EXPERIMENTAL

Cryptands C222, C221, C211 and C22 (1,10-diaza-18-crown-6) were of the highest purity available from Merck Chemical Company. Cryptands C222 and C22 were recrystallized from reagent grade *n*-heptane and vacuum dried over P_2O_5 for 72 h. Reagent grade murexide (Merck), calcium nitrate (BDH), strontium nitrate and barium nitrate (both from Fluka) were used without further purification except for vacuum drying over P_2O_5. Dimethylsulfoxide for spectroscopic use (DMSO, Merck) was used as received.

All spectra were obtained with a Philips PUB700 spectrophotometer and absorbance measurements were made with a Metrohm 662 photometer at 25.0, 35.0, 45.0, and 55.0°C. At all temperatures, the cell was thermostatted with a Lo-Temtrol 154 thermostat to $\pm 0.1\,^\circ\mathrm{C}$.

Formation constants of the 1:1 complexes between metal ions and murexide (Mu, as coloured ligand) and cryptand (L, as buffer ligand) were determined by absorbance measurements, at λ_{max} of metal ion-murexide complex, of solutions in which constant concentrations of both ligands (3.0×10^{-5} M murexide and 5×10^{-5} M cryptand) were titrated with a concentrated metal ion solution in DMSO (1.0×10^{-2} M) using a pre-calibrated microlitre syringe. Attainment of equilibrium was checked by observation of no further change in spectra after several hours.

When an alkaline earth cation reacts with murexide, Mu, and a cryptand, L, to form 1:1 complexes, the corresponding formation constants are given as

$$M + Mu = MMu \quad K_{MMu} = [MMu]/[M][Mu] \tag{1}$$

$$M + L = ML \quad K_{ML} = [ML]/[M][L] \tag{2}$$

(charges are omitted for simplicity). Mass balance equations and the observed absorbance, A_{obs}, are given as

$$CMu = [Mu] + [MMu] \tag{3}$$

$$CL = [L] + [ML] \tag{4}$$

$$CM = [M] + [MMu] + [ML] \tag{5}$$

$$A_{obs} = \varepsilon_{Mu}[Mu] + \varepsilon_{MMu}[MMu] \tag{6}$$

where C and ε values are the analytical concentration and molar absorptivity of the species indicated, respectively. The mass balance equations can be solved in order to obtain an equation for the free metal ion concentration, [M], as

$$K_{MMu}K_{ML}[M]^3 - \{K_{MMu}K_{ML}(C_M - C_{Mu} - C_L) - K_{MMu} - K_{ML}\}[M]^2 - \{K_{ML}(C_M - C_L) + K_{MMu}(C_{Mu} - C_M) - 1\}[M] - C_M = 0 \qquad (7)$$

For evaluation of the formation constants from the absorbance *vs* C_M/C_{Mu} mole ratio data, a non-linear least-squares curve fitting program, KINFIT, was used.[18] The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique[19] or the Powell procedure.[20] Adjustable parameters are the formation constants K_{MMu} and K_{ML} and molar absorptivities ε_{Mu} and ε_{MMu}.

The free metal ion concentration was calculated from equation (*7*) by means of a Newton-Raphson procedure. Once the value of [M] had been obtained, the concentrations of all other species involved were calculated from the mass balance equations (*3*) to (*5*) by using the estimated values of the formation constants and molar absorptivities at the current iteration step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of absorbance for all experimental points is minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of data.

RESULTS AND DISCUSSION

The visible spectra of murexide and its alkaline earht complexes in DMSO have already been reported.[21] All of the complexes are distinguished by a strong shift in comparison to the free murexide. Reasons for such strong and ion-specific blue shifts are discussed elsewhere.[21–23] It is well known that murexide forms a 1:1 complex with various metal ions in DMSO solution.[21,22,24]

The formation constants of Ca^{2+}, Cr^{2+} and Ba^{2+} complexes with murexide and different cryptands used were obtained at various tempeatures by absorbance measurements, at λ_{max} of the murexide complexes, of solutions in which varying concentrations of metal ions were added to fixed amounts of murexide and cryptands in DMSO solution. All the resulting formation constants, evaluated from computer fitting of the absorbance-mole ratio data, are summarized in Table 1. The relationship between the stabilities of alkaline earth cryptates and the crystal radii of the metal ions[25] is shown in Figure 2.

In order to achieve a better understanding of the thermodynamics of complexation, it is useful to consider the enthalpic and entropic contributions to these reactions. These thermodynamic parameters were calculated from the temperature dependence of the complex formation constants. Plots of log K_f *vs* 1/T in all cases were linear and the $\Delta H°$ and $\Delta S°$ values were determined in the usual manner from the slope and intercept of the plots, respectively. The results also are included in Table 1.

The data show a decrease in the stability of the resulting murexide complexes in the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$. The same stability order has been reported previously in different solvents.[21,26] The data also show that all three murexide

Table 1 Stability constants (log K_f; K_f in M^{-1}) and thermodynamic parameters ($\Delta H°$ in kJ mol^{-1}; $\Delta S°$ in J mol^{-1} K^{-1}) for the reaction of alkaline earth ions with murexide and different cryptands in DMSO solution

Ligand	Ion	Log K_f					
		25 °C	35 °C	45 °C	55 °C	$-\Delta H°$	$\Delta S°$
Murexide	Ca^{2+} (1.00 Å)[a]	4.73±0.03	4.66±0.03	4.62±0.02	4.58±0.03	8.8±0.2	60.7±0.4
	Sr^{2+} (1.18Å)[a]	4.67±0.02	4.61±0.02	4.56±0.03	4.51±0.02	10.0±0.2	56.5±0.3
	Ba^{2+} (1.35 Å)[a]	4.41±0.02	4.37±0.02	4.30±0.03	4.24±0.02	10.9±0.2	48.5±0.7
C211 (0.8 Å)[b]	Ca^{2+}	2.81±0.04	2.75±0.03	2.70±0.03	2.65±0.03	10.0±0.2	20.5±0.2
	Sr^{2+}	2.78±0.04	2.69±0.04	2.61±0.03	2.56±0.02	13.8±0.2	6.7±0.7
	Ba^{2+}	2.57±0.03	2.54±0.04	2.51±0.03	2.47±0.03	6.3±0.1	28.9±0.3
C221 (1.1 Å)[b]	Ca^{2+}	3.67±0.02	3.55±0.02	3.44±0.02	3.33±0.04	21.3±0.2	0.8±0.1
	Sr^{2+}	5.19±0.04	5.10±0.04	4.98±0.03	4.89±0.06	19.2±0.2	35.6±0.7
	Ba^{2+}	4.12±0.04	4.06±0.03	3.94±0.03	3.82±0.03	18.8±0.6	15.9±1.8
C222 (1.4 Å)[b]	Ca^{2+}	2.03±0.05					
	Sr^{2+}	4.44±0.02	4.37±0.02	4.30±0.02	4.24±0.03	13.0±0.2	42.3±0.3
	Ba^{2+}	5.02±0.05	4.93±0.03	4.86±0.04	4.74±0.03	16.7±0.4	40.6±1.2
C22 (1.3-1.8 Å)[c]	Ca^{2+}	2.40±0.04	2.31±0.04	2.24±0.03	2.10±0.02	19.2±0.5	-18.4±1.7
	Sr^{2+}	2.58±0.02	2.55±0.02	2.45±0.02	2.33±0.02	16.3±0.7	-4.2±2.3
	Ba^{2+}	2.68±0.03	2.64±0.02	2.56±0.02	2.38±0.02	18.4±1.1	-9.6±2.5

[a] Ionic radius, ref. 25. [b] Cavity radius, ref. 5. [c] Cavity radius, ref. 7.

complexes are stabilized by both enthalpy and entropy terms. The sign and magnitude of the $\Delta S°$ values are consistent with the "chelate effect".[27]

Ca^{2+}: C221 > C211 > C22 > C222

Sr^{2+}: C221 > C222 > C211 > C22

Ba^{2+}; C222 > C221 > C22 > C211

It is immediately obvious that macrobicyclic ligands from the most stable complexes with alkaline earth cations, in comparison with those obtained with macrocycle C22. Highest stabilities are found for [$Sr^{2+} \subset$ C221] (strontium ion included in cryptand C221) and [$Ba^{2+} \subset$ C222]. It is well known that spherical alkali and alkaline earth cations form very stable "inclusion" complexes of the cryptate type with cryptand molecules of proper size in which the cation is located in the centre of the cryptand cavity and effectively isolated from solvent molecules.[5,6,28] From the data, it is seen that the high stabilities of the above complexes correspond to the preferred complexation of those alkaline earth cations whose size closely fits the intermolecular cavity of cryptands.

It is interesting to note that, although the ring size of C222 is about the same as the cavity of cryptand C222, its Ba^{2+} complex is more than two orders of magnitude weaker than that with C222. The results clearly indicate a pronounced "cryptate effect," brought about upon connection of a $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ bridge onto the macrocyclic ring of C22 to form the macrobicyclic ligand C222. From Table 1 it is seen that while the H° values for the formation of both complexes are negative in sign and about the same in magnitude (within experimental error), the corresponding S° values are quite different both in sign and magnitude (*i.e.*, -9.6 e.u. for C22 complex and +40.6 e.u.

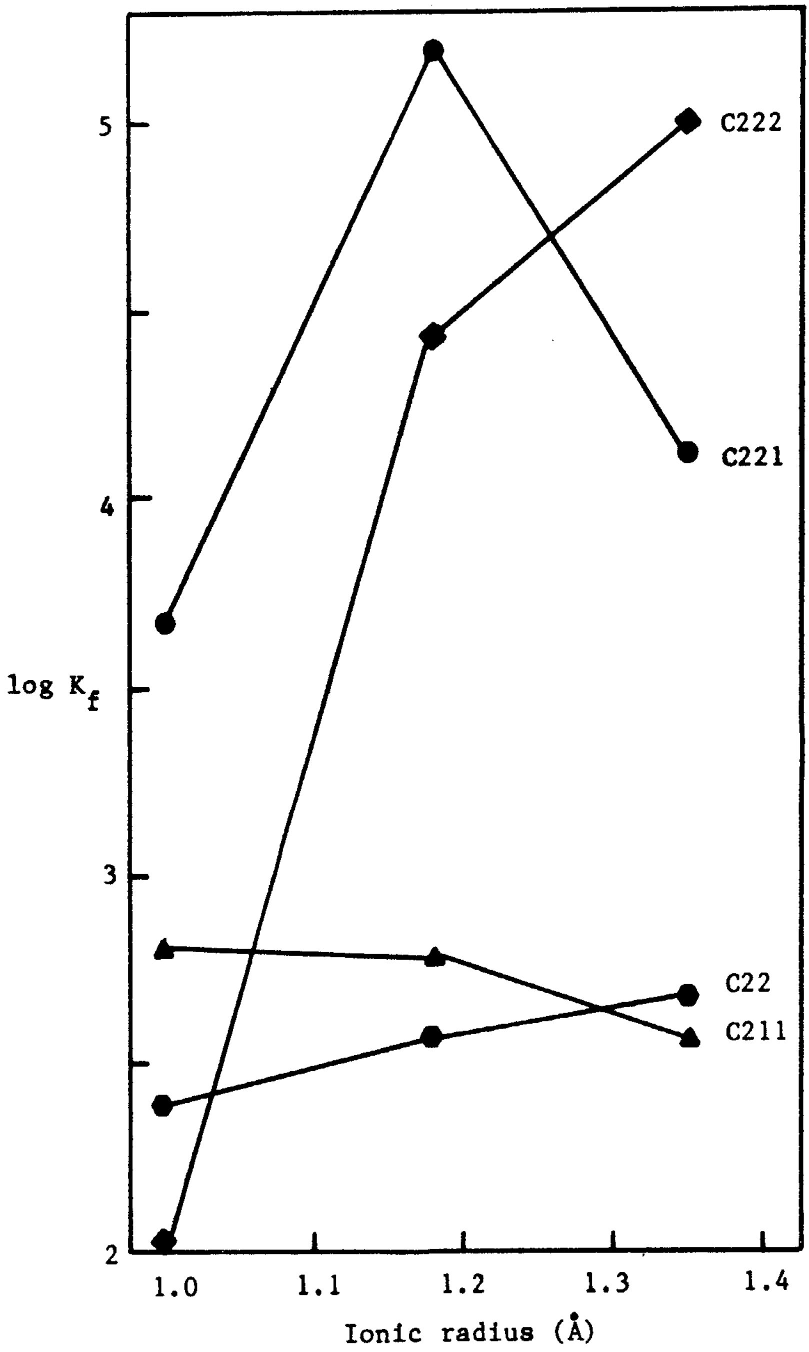

Figure 2 Stability constants for different alkaline earth cryptates *vs* ionic radii of the cations.

for C222 cryptate). The results clearly emphasize that the observed cryptate effect is only caused by favourable entropic contributions. Similar results were reported previously.[29] The same conclusion can be reached from a comparison of the enthalpy and entropy changes for the complexation of strontium ion with C22 and C222.

In complex formation, the three-dimensional cavities of cryptands allow for maximum replacement of the DMSO molecules in the inner coordination shell of the metal ions by the donating centres of the ligand. In addition, very little conformational rearrangement is required, compared to the flexible C22 molecule, due to rigid cryptand structure. Thus, the observation of a large and positive entropy change during cryptate formation is not surprising. On the other hand, the crown ether C22 can only hold the cation in a two-dimensional cavity, allowing some direct interactions between DMSO molecule and the complexed cation. Moreover, the decrease in entropy upon complexation in this case can also be related to a change in the conformational entropy of the ligand C22, from a rather flexible structure in the free state to a rigid structure in the complexed form.[30,31]

It should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the cryptates, as determined by the relative sizes of the cation and cryptand cavity, but a measure of the relative strength as compared to ionic solvation. For the case of alkaline earth cations the free energy of solvation increases continuously as the size of the cations decreases.[32,33]

Since the rigid cryptand molecules have cavities of fixed size, the maximum free energy of complexation is attained when the cation can closely fit the cavity. If the cation is too small for the cryptand cavity (*e.g.*, Ca^{2+}-C222 system), it is expected to have a lower interaction energy since the cavity cannot contract. In such a case, considering the low binding energy of cryptate and the high solvation energy of the cation, it is not unexpected to observe the formation of a rather weak complex. Cations of larger size than the cryptand's cavity are also expected to have a lower free energy of complexation. In this case, the cation can only partially penetrate the cavity to form an "exclusive" complex in which the cation remains exposed to solvent molecules. Evidence for the formation of such "exclusive" cryptates has already been reported.[34] As is obvious from the data in Table 1, the low stability constants of the resulting complexes originates from unfavourable ΔH° and/or small ΔS° values of the corresponding complexation reactions.

The particular three-dimensional structure of the cryptands shows up clearly in two aspects of the resulting alkaline earth cryptates: a very high stability and a high selectivity among the cations. Figure 2 shows that in the case of C221 and C222 cryptates, a pronounced cation selectivity (peak selectivity) is found among the metal ions. The rigid cryptand molecules are able to discriminate against cations of larger or smaller sizes than their cavities, since distortion of the ligands either by expansion or contraction results in a considerable destabilization.[5,6,35] On the other hand, Figure 2 shows that in the case of C22 and C211 ligands, the resulting complexes with alkaline earth ions are not only relatively weak, but also that there is only minor selectivity (plateau selectivity) for Ba^{2+} and Ca^{2+} ions. It seems reasonable to assume this selectivity behaviour of C22 is a result of its high flexibility in solution, in comparsion with the rigid bicyclic cryptand molecules. It is interesting to note that in the case of cryptand C211, despite its high rigidity, the ligand cannot discriminate against the cations. This is most probably because of the small cavity size of C211 for the cations used, which also results in both unfavourable enthalpy and entropy changes upon complexation.

It should be noted that the thermodynamic parameters for the complexation of alkaline earth cations with cryptands have been previously reported in water[36,37] and methanol solution.[38,39] Comparison of the data obtained in this work with those reported, reveal that the formation constants of alkaline earth cryptates are sensitive to solvent variation; in all cases, stability decreases in the order MeOH > H_2O > DMSO.

The solvating ability of the solvents increases in a somewhat similar order.[15] Solvent dependence of K_f values arises from variation in solvation of free cations, cryptands and resulting complexes. It has been shown that interactions between solvent molecules and cryptands are small and do not make a large contribution to the variation in K_f.[40,41] Depending upon how effectively the cation in the cryptate is shielded from the solvent, it can be expected that the solvation of cryptate may have some contribution to the stability in a few cases (*i.e.*, when the cation is too large and can only partially penetrate the cavity). Thus desolvation of the M^{2+} ion would dominate stability behaviour.

It is interesting to note that, in most cases, the $\Delta S°$ values in MeOH[40,41] and H_2O[38,39] are much more positive than those in DMSO, as reported in this paper. Since the cryptand cavity allows for maximum replacement of solvent molecules in the inner coordination sphere of the cations by the donor atoms of the ligands,[5,6] this considerable variation in entropy can be related to the desolvation of the cations during cation inclusion. The release of a larger number of MeOH and, especially, H_2O molecules from the first coordination shell of the cations (compared with bulkier DMSO molecules),[32,42,43] brought about upon complexation, might be the main reason for the larger $\Delta S°$ contribution to the stability of resulting cryptates in water and methanol solutions.

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