

# Complexation thermodynamics of some alkali-metal cations with 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane in Acetonitrile

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**Abstract** The interaction of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) with alkali-metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in aprotic medium (acetonitrile) has been investigated. Conductance measurements demonstrated that 1:1 metal cation:ligand stoichiometries are found with these cations in this solvent.  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR experiments were carried out by titration of the metal cation solutions with Kryptofix5 solution in  $\text{CD}_3\text{CN} + \text{CH}_3\text{CN}$  at 298 K. Thermodynamic parameters of complexation for this ligand and alkali-metal cations in acetonitrile at 278–308 K were derived from titration conductometry. The highest stability is found for sodium complex. The complexation sequence, based on the value of  $\log K$  at 278–308 K was found to be  $\text{Na}^+ > \text{K}^+ > \text{Li}^+$ .

**Keywords** Thermodynamics · 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane · Kryptofix5 · Conductometry · NMR · Stability constant

## Introduction

Cryptands (trade name Kryptofix) are cyclic or polycyclic molecules which contain three or more binding sites held together by covalent bonds. These molecules are three dimensional analogues of crown ethers. These complexing agents display a wide range of binding specificities, and the association properties of crown ethers with alkaline cations have been mainly described

in terms of similarities between the cation size and the size of the inner hole of the crown ether [1, 2].

Some Kryptofixes are used to produce  $^{18}\text{F}$ -Pharmaceuticals [3–6].  $^{18}\text{F}$ -labelled compounds are most widely used radiopharmaceuticals, since half-life of  $^{18}\text{F}$  (110 min) is long enough to synthesize labeled compounds and to use those for routine clinical purposes.

Addition of some Kryptofixes to proteases considerably enhances the activity of these enzymes in transesterification reactions of some esters in organic solvents [7]. Results from literatures suggest that Kryptofixes could be effective chelators to reduce the body burden of some metal cations following an acute oral exposure to these elements [8, 9].

Crown ethers were found to show significant anti-fungal activity against some wood-decay fungi, phytopathogenic fungi [10].

These applications originated in complexation behavior of these compounds. This behavior of lanthanides, alkali, and alkaline earth metal ions with crown ethers have been extensively studied in various solvents [11–15]. Most of these researches in the area of complexation of metal ions with crown ethers have been carried out to determine stability constants or/and  $\Delta H^\circ$  and  $\Delta S^\circ$  at 298 K in pure or mixed solvents by the classical methods, but relatively few have dealt with the effect of changes in temperature by NMR technique [16, 17].

In this paper, the thermodynamic behavior of complexation of the  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  by Kryptofix5 are studied by conductance titration in acetonitrile (AN). To proceed with this evaluation, NMR titration is used to derive the stability constants ( $\log K$ ) of related crown ether and alkali metal ions in AN.

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## Experimental

### Materials

Acetonitrile (AN) (99.5%), deuterated acetonitrile, (>99.0%) Kryptofix5 (K5) or 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (>99.0%),  $\text{KClO}_4$  (99.5%) and  $\text{NaClO}_4$  (99.0%) were of Merck except  $\text{LiClO}_4$  (99.0%) (Fluka) and were used without additional purification.

### Apparatus

Conductance measurements were carried out using a conductivity meter (WPA, CMD500). The conductivity meter was equipped with a dip-type cell (EL 178) of cell constant  $1.0 \text{ cm}^{-1}$ . The temperature of the water bath (Julabo, F12) was controlled at  $\pm 0.1 \text{ }^\circ\text{C}$ . The cell was calibrated using KCl solutions. Duplicate measurements of each solution were made. All molar conductivities were calculated from specific conductivities. The results varied within  $\pm 0.1\%$ .

NMR measurements were carried out with a Bruker Avance 300 spectrometer with the processing software XWIN-NMR version 3.1. All measurements were done in AN + AN- $d_3$  at 298 K. Five millimeter NMR tubes were used. A Hamilton syringe was used to addition of ligand solution.

### Procedure for conductometry

The metal perchlorate solution ( $1.0 \times 10^{-5} \text{ M}$ ) was placed in the cell, and the conductivity was measured. Kryptofix5 solution ( $1.0 \times 10^{-3} \text{ M}$ ) was added to the cell. The conductivity was measured after each addition as above. These procedures were carried out at 278, 288, 298 and 303 K.

### Procedure for NMR

NMR titration of Kryptofix5 solution with  $\text{LiClO}_4$  and  $\text{NaClO}_4$  solutions at 298 K done using  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR spectra were recorded on a Bruker 300 spectrometer operating at 116.64 and 79.90 MHz, respectively.

A  $90^\circ$  pulse of  $9.52 \mu\text{s}$  was used in the case of the  $^7\text{Li}$  NMR spectra. All chemical shifts were referenced against the  $1.0 \times 10^{-2} \text{ M}$  stock solution of metal perchlorate in 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ , used throughout this study, at 298 K. The chemical shift of this stock solution is  $-2.09 \text{ ppm}$  referenced to a 4.0 M LiCl solution in  $\text{D}_2\text{O}$ . The acquisition time was 7.03 s,

corresponding to sweep widths of 2.33 kHz. The relaxation time was 1.0 s. Typically, the number of scans was 4.

Also, a  $90^\circ$  pulse of  $6.0 \mu\text{s}$  was used in the case of the  $^{23}\text{Na}$  NMR spectra. All chemical shifts were referenced against the  $1.0 \times 10^{-2} \text{ M}$  stock solution of metal perchlorate in 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ , used throughout this study, at 298 K. The chemical shift of this stock solution is  $-6.82 \text{ ppm}$  referenced to a 4.0 M NaCl solution in  $\text{D}_2\text{O}$ . The acquisition time was 1.72 s, corresponding to sweep widths of 9.52 kHz. The relaxation time was 2.0 s and the number of scans was 64–2000.

All shifts were accurate to  $\pm 0.01 \text{ ppm}$ . Temperature was measured to a precision of  $\pm 1 \text{ K}$ .

The metal perchlorate solution ( $1.0 \times 10^{-2} \text{ M}$ ) was placed in the NMR tube, and the chemical shift and frequency were measured. Kryptofix5 solution ( $5.0 \times 10^{-2} \text{ M}$ ) was added to the NMR tube. The chemical shift and frequency were measured after each addition as above.

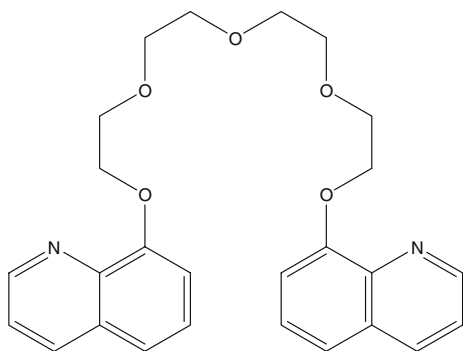
### Stability constants calculations

The evaluations of stability constants with the *Non-linear Least Square Curve Fitting* program KINFIT were performed according to the procedure described in ref. 18.

## Results and discussion

There are several techniques currently used for the determination of stability constant data for complexation reactions involving metal cations and macrocyclic ligands [19–27]. However, the suitability of the technique is largely dependent on the magnitude of the stability constant. One of the main advantages of titration conductometry is determination of thermodynamic functions  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the complexation of Kryptofix5 (Fig. 1) with alkaline cations, namely,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , that in this work have calculated using the determined stability constants in the temperature range 278–303 K in solutions containing 100 volume % of acetonitrile.

The plot of the composition of lithium, sodium and potassium complexes of Kryptofix5 that were investigated by conductance measurements gave a break at ligand-metal ion concentration ratios equal to unity, which shows that, in this solvent, 1:1 metal ion-crown complexes are only formed. Figure 2 shows the plots of the conductance titration of these complexations at 278 K. Ionic molar conductances  $\lambda^\circ$  of lithium, sodium

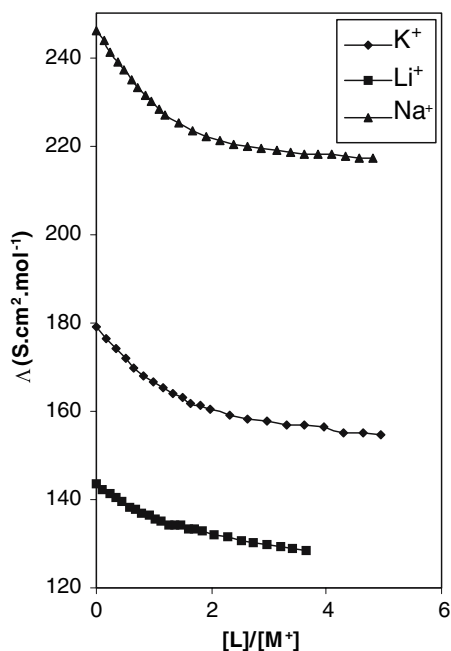


**Fig. 1** Structure of Kryptofix5

and potassium complex with K5 in AN at all temperatures ( $\lambda^\circ$  ( $\text{Li}^+$ -K5));  $\lambda^\circ$  ( $\text{Na}^+$ -K5));  $\lambda^\circ$  ( $\text{K}^+$ -K5)) are lower than that for the free cations ( $\lambda^\circ$  ( $\text{Li}^+$ ),  $\lambda^\circ$  ( $\text{Na}^+$ ),  $\lambda^\circ$  ( $\text{K}^+$ )) in the same solvent and at the same temperature which originated in lower mobility of these complexes than that for free cations.

Table 1 lists stability constants of these complexes in AN at 278–303 K using conductometry obtained by computer fitting of the molar conductance-mole ratio data [18]. A sample computer fit of these data is shown in Fig. 3.

The data reported in Table 1 refer to the following process in solution



**Fig. 2** Molar conductance of the complex species as a function of K5:cation concentrations ( $[\text{L}]/[\text{M}^+]$ ) in 100% acetonitrile at 278 K

The stability constant  $K$  for reaction 1 is given by

$$K = \frac{[\text{ML}^+]}{[\text{M}^+][\text{L}]} \frac{\gamma_{\text{ML}^+}}{\gamma_{\text{M}^+}\gamma_{\text{L}}} \quad (2)$$

where  $[\text{ML}^+]$ ,  $[\text{M}^+]$ ,  $[\text{L}]$ , and  $\gamma$  denote the concentration of the complex, uncomplexed cation, uncomplexed crown ether, and the activity coefficient of the species indicated, respectively. Since this work has been performed in dilute solutions, it is assumed that the ratio of activity coefficients is unity.

The change of the topology of the ligand from a linear conformation in the uncomplexed state to a helical conformation in the complex state leads to a large loss of entropy. This is supported by the experiment finding that the decrease of entropy due to complexation is smallest for the uptake of those cations, which do not induce steric deformation of the ligand structure [28].  $\text{Na}^+$  ion fit well into the sterically optimum cavity of ligand K5. Thus, the favored stability of the  $\text{Na}^+$  complex of ligand K5 is the consequence of the absence of a destabilizing loss of entropy [28].

To calculate the thermodynamic functions for the complexation process at different temperatures, the van't Hoff equation was used.

$$\log K = -\Delta H^\circ/2.303RT + \Delta S^\circ/2.303R \quad (3)$$

Using the well-known thermodynamic relationship

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (4)$$

the standard Gibbs energy of complex formation,  $\Delta G^\circ$  can be calculated.

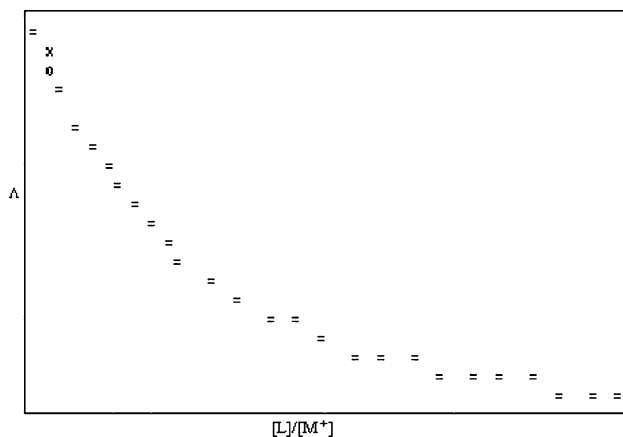
Table 1 also illustrates the influence of the cation size on  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the ligand measured. The values of  $\Delta H^\circ$  become more negative with increasing ionic radius. The changes of the enthalpy of the ligand by complexation are mainly due to the changes of solvation, intermolecular ligand-ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bound metal ion [29].

It is important to discuss these results in terms of the factors which contribute to the selective complexation of macrocycles and metal cations. Among these are the nature of the donor atoms, the effect of the substituent in the crown ether, and the nature of the solvent.

The thermodynamic data reflect the effect of the donor atoms of the ligand in the complexation process involving the solvent. Thus, the active sites of complexation are provided by nitrogen and ethereal

**Table 1** Stability constants and thermodynamic parameters at 278–308 K for the complexation of Kryptofix5 with Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> cations in acetonitrile using conductometry

Cations	logK				$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )
	5 °C	15 °C	25 °C	35 °C			
Li <sup>+</sup>	4.24 ± 0.03	4.17 ± 0.05	4.09 ± 0.08	4.03 ± 0.03	-11.6 ± 0.5	39.3 ± 2.0	-23.0 ± 0.7
Na <sup>+</sup>	4.74 ± 0.08	4.64 ± 0.04	4.57 ± 0.01	4.48 ± 0.07	-14.0 ± 0.4	40.6 ± 1.0	-25.6 ± 0.6
K <sup>+</sup>	4.67 ± 0.03	4.54 ± 0.02	4.36 ± 0.02	4.16 ± 0.03	-28.0 ± 3.0	-10.6 ± 9.0	-24.9 ± 4.0

**Fig. 3** Computer fit of molar conductance of the complex species as a function of K5:Na<sup>+</sup> concentrations ( $[L]/[M^+]$ ) in 100% acetonitrile at 278 K

oxygen donor atoms of K5. These sites afford a much stronger dipolar interaction as reflected in the higher stabilities of Kryptofix5 with sodium cation in solvent relative to lithium and potassium cations [30].

Since, in the complexation reactions, the ligand must compete with solvent molecules for cations the use of solvents of low solvating ability is expected to lead greater stability. Because of low stabilities in water and high donicity solvents, we chose to study crown ether complexation of the metal cations in acetonitrile, a solvent with a moderate dielectric constant (36.64). Moreover, de Nomor et al. have shown that, in acetonitrile, the perchlorate anion is not associated with the sodium cation complexed by some crown ethers [23]. Table 2 shows a comparison of the stability constant of ligand K5 with Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> in methanol [31] and acetonitrile.

Plots of log K versus 1/T in 100 volume % of acetonitrile for the crown ether with all cations studied were linear (Fig. 4). According to these plots, the stability constant K decreases with increasing temperature. This indicates that the complexation process is exothermic.

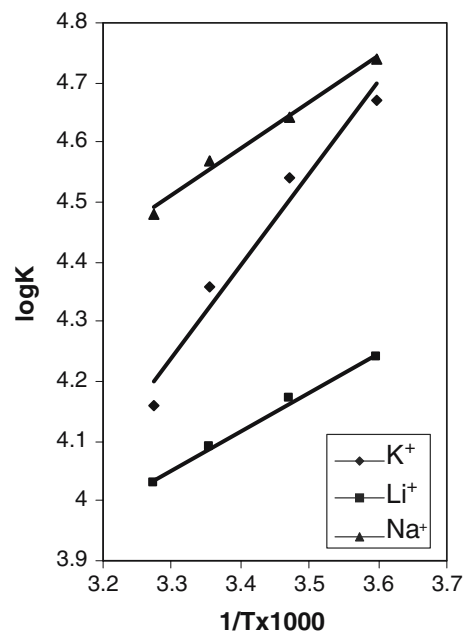
For comparison purposes, NMR methods have carried out and data for complexation of Kryptofix5 with

**Table 2** Stability constants at 298 K for the complexation of Kryptofix5 with Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> in different solvents

Cations	logK		
	Ref. 31	This work: conductometry	This work: NMR
Li <sup>+</sup>	2.37	4.09 ± 0.08	4.58 ± 0.08
Na <sup>+</sup>	3.22	4.57 ± 0.01	4.70 ± 0.06
K <sup>+</sup>	3.51	4.36 ± 0.02	–

lithium and sodium salts at 298 K have reported in Table 2.

According to Figs. 5 and 6, the relative intensity of the broad signal increases with an increase of  $\rho$ , defined as  $\rho = [K5]_{tot}/[cation\ perchlorate]_{tot}$ , while the signal of the solvated sodium or lithium remains narrow. For values of  $\rho$  larger than 1, a single broad peak is observed. In all cases, evaluation were observed, indicating that the exchange rate of the cation between the bulk solution and the complexed site is fast on the NMR time scale in room temperature.

**Fig. 4** logK of complexation of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> with K5 in acetonitrile as a function of 1/T

**Fig. 5**  $^7\text{Li}$  NMR spectra of 10 mM  $\text{LiClO}_4$  in the presence of various amounts of K5 at 298 K ( $\rho = [\text{K5}]_{\text{tot}}/[\text{LiClO}_4]_{\text{tot}}$ )

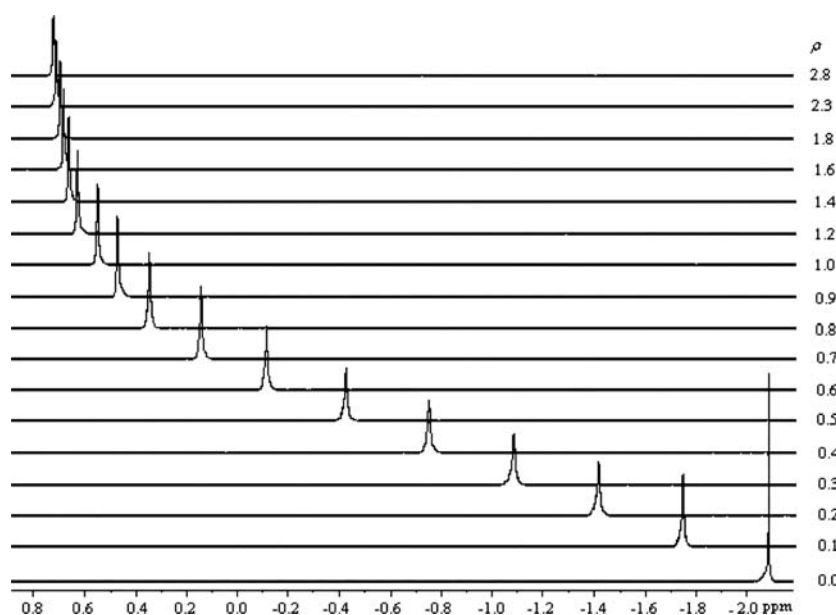


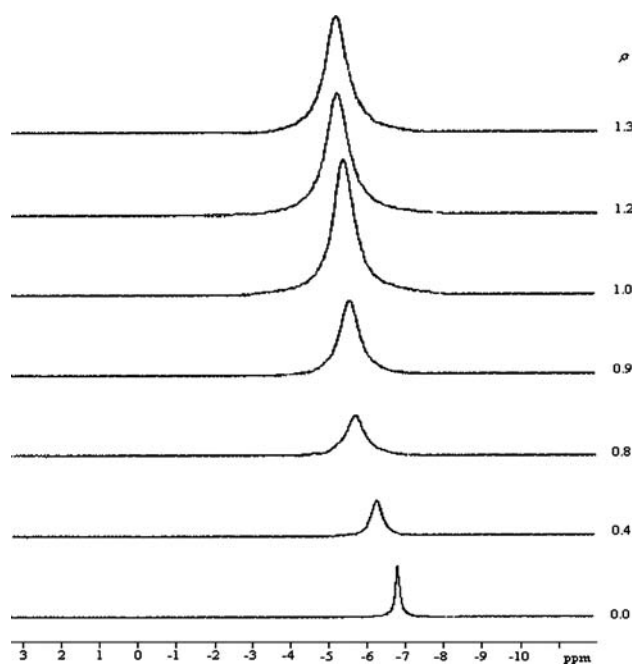
Figure 5 shows the  $^7\text{Li}$  NMR spectra of a  $1.0 \times 10^{-2}$  M solution of lithium perchlorate at 298 K, in a mixture of 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ , in the absence and in the presence of increasing quantities of  $5.0 \times 10^{-2}$  M solution of K5 in a mixture of 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ . In the presence of K5, a line, attributed to a 1:1 complex lithium ion-K5, is observed about 0.55 ppm downfield from the signal of the solvated lithium at  $-2.09$  ppm.

Figure 6 shows the  $^{23}\text{Na}$  NMR spectra of a  $1.0 \times 10^{-2}$  M solution of sodium perchlorate at 298 K, in a mixture of 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ , in the absence and in the presence of increasing quantities of  $5.0 \times 10^{-2}$  M solution of K5 in a mixture of 75:25 v:v  $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ . In the limits of the experimental error, the chemical shifts of solvated sodium remain constant, while a small, but systematic, variation of the chemical shifts of the complexed sodium is observed. For example, the chemical shift of  $\text{Na}^+\text{-K5}$ , obtained for  $\rho = 0.4$ , is  $-6.29$  ppm at 298 K. It shifts regularly to a value of  $-5.37$  ppm for  $\rho = 1.3$ . In the presence of K5, a broad line, attributed to a 1:1 complex sodium ion-K5, is observed about  $-5.52$  ppm downfield from the signal of the solvated sodium at  $-6.82$  ppm.

As Table 2 has been reported there are good agreements between the log K values for complexation of lithium and sodium in AN at 298 K using conductometry and NMR methods.

## Conclusions

Conductance and NMR measurements demonstrated 1:1 metal cation:ligand stoichiometries in acetonitrile.



**Fig. 6**  $^{23}\text{Na}$  NMR spectra of 10 mM  $\text{NaClO}_4$  in the presence of various amounts of K5 at 298 K ( $\rho = [\text{K5}]_{\text{tot}}/[\text{NaClO}_4]_{\text{tot}}$ )

Stability constants for these complexes were evaluated with nonlinear least square curve-fitting program. The highest stability is found for sodium. Thus, sodium ion is sterically well fitted into the cavity of ligand K5 in this solvent. Furthermore, the thermodynamic data reflect the participation of seven heteroatoms (5O, 2N) in the complexation is exothermic. These sites cause a much stronger dipolar interaction as reflected in the higher stabilities of Kryptofix5 with sodium cation in the solvent relative to lithium and potassium cations.

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