ELSEVIER

Coordination Chemistry Reviews
174 (1998) 179–189

COORDINATION CHEMISTRY REVIEWS

Approaches to improvement of metal ion selectivity by cryptands

Xian Xin Zhang, Reed M. Izatt *, Jerald S. Bradshaw,
Krzysztof E. Krakowiak [1]

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700, USA

Received 12 August 1997; accepted 30 November 1997

Contents

Abstract 179
1. Introduction 180
2. Size-match relationship 180
3. Symmetry of cryptands 181
4. Replacement of ethylene by propylene 184
5. Cryptands containing benzo and several other substituents 186
Acknowledgements 188
References 188

Abstract

Several approaches to improvement of metal ion selectivity by mixed oxygen–nitrogen donor cryptands are discussed. Because of the relatively rigid structures of cryptands, thermodynamic stabilities of the cryptate complexes strongly depend on the match of the cation size and cryptand cavity diameters. Symmetry is an important factor influencing the properties of cryptand complexation. One rule to improve metal ion selectivity by oxygen–nitrogen donor cryptands is to obtain the ligand that has the best size-match cavity with the cation while keeping a symmetric spherical-coordination array. High selectivity for a small cation can be obtained when the cryptand is able to form a number of six-membered chelate rings with the metal ion while the requirements of the high-symmetric donor atom array and size-matched cavity are met. On the other hand, introduction of benzene rings and other groups to cryptands usually decreases metal ion binding and selectivity. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cryptand; Equilibrium constant; Alkali metal ion complex; Alkaline-earth metal ion complex

---

* Corresponding author. Tel: +1 801 378 2315; Fax: +1 801 378 5474; e-mail: izattr@vanlab.byu.edu
[1] Present address: IBC Advanced Technologies, Inc, PO Box 98, American Fork, UT 84003, USA.

PII S0010-8545(98)00050-2

1. Introduction

Macrobicyclic ligands, such as cryptand [2.2.2], contain two bridgehead atoms (nitrogen, carbon, phosphorus, etc.) connected by three bridges [1]. They are usually spherical and capable of encapsulating metal ions in their cage-like cavities to form stable complexes. Since the synthesis of the first cryptand [2.2.2] in 1968 by Lehn and co-workers [1–3], a large number of macrobicyclic and macropolycyclic compounds have been prepared and their complexation properties studied. Extensive reviews have been published [1,4–16]. Although we will mention some results from these publications, the purpose of this article is not to reiterate the properties of cryptands but to discuss several approaches to the improvement of metal ion selectivity by cryptands. Our attention is focused on several new cryptands which show high metal ion selectivity. The cryptands discussed in this article contain both oxygen and nitrogen donors and have nitrogen as the bridgehead atom. Cryptands containing all nitrogen donors and other heteroatoms (such as sulfur and phosphorus) are not included.

2. Size-match relationship

The three-dimensional cavity of the cryptands results in a relatively rigid structure and the thermodynamic stabilities of the cryptate complexes strongly depend on the match of the cation size and cryptand cavity diameters [1–16].

Equilibrium constants (log *K*) in Table 1 for complexation of alkali and alkaline-earth metal ions with cryptands having different cavity sizes illustrate the size-match relationship [17–19]. The cavity radius of the smallest cryptand [1.1.1] (~0.5 Å) is even too small for Li^+ (ionic radius, 0.60 Å). The stability of the [1.1.1]–Li^+ complex is low. However, [1.1.1] still selects Li^+ over Na^+ and Ca^{2+}. Cryptand [2.1.1] has

Table 1
Log *K* values for the interactions of cryptands with metal ions[a]

	Li^+ (0.68)	Na^+ (0.95)	K^+ (1.33)	Rb^+ (1.48)	Cs^+ (1.69)	Mg^{2+} (0.66)	Ca^{2+} (0.99)	Sr^{2+} (1.13)	Ba^{2+} (1.35)
[1.1.1][b] (~0.5)	1.7	0.8	–	–	–	–	1.3	–	–
[2.1.1][c] (0.8)	5.5	3.2	<2	<2	<2	2.5	2.50	<2	<2
[2.2.1][c] (1.1)	2.50	5.40	3.95	2.55	<2	<2	6.95	7.35	6.30
[2.2.2][c] (1.4)	1.25	3.9	5.4	4.35	<2	<2	4.4	8.0	9.5
[3.3.2][d] (2.1)	–	3.2	6.0	6.15	>6	–	–	–	–
[3.3.3][d] (2.4)	–	2.7	5.4	5.7	5.9	–	–	–	–

[a] Values (in Å) of radii of cryptand cavities and of metal ions (in parentheses) are from Ref. [13] and Handbook of Chemistry and Physics, R.C. Weast (ed.), 66th ed., CRC Press, Boca Raton, FL, 1985, p. F-164.

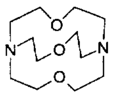
[b] Ref. [18]. Determined in dimethylformamide at 20 °C.

[c] Refs. [17,19]. Determined in water at 25 °C.

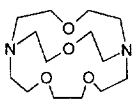
[d] Ref. [17]. Determined in methanol at 25 °C.

a cavity radius of 0.8 Å which is a little larger than the ionic radius of Li^+ but smaller than that of Na^+ and other alkali metal ions. As a result, [2.1.1] forms the most stable complexes with Li^+ ($\log K(H_2O) = 5.5$) among these cations. Cryptand [2.2.1] has a cavity radius which matches the ionic radius of Na^+ and it selectively binds Na^+ ($\log K(H_2O) = 5.40$) over all other alkali metal ions. In addition, the close match between the cavity radius of [2.2.1] and the ionic radii of Ca^{2+} and Sr^{2+} causes the larger $\log K$ values for the interaction of [2.2.1] with Ca^{2+} and Sr^{2+} than with Ba^{2+}. The cavity radius of cryptand [2.2.2] (1.4 Å) is close to the ionic radii of K^+ (1.33 Å) and Ba^{2+} (1.35 Å) and it shows a high selectivity for K^+ and Ba^{2+} over the other alkali and alkaline-earth metal ions.

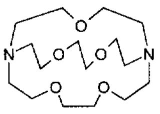
Large-size cryptands [3.3.2] and [3.3.3] form more stable complexes with large cations (Rb^+ and Cs^+) than with small ones. However, the cavity radii of [3.3.2] and [3.3.3] (2.1 and 2.4 Å, respectively) are too large to match the ionic radii of Rb^+ and Cs^+ (1.48 and 1.69 Å, respectively), resulting in low selectivity for Rb^+ and Cs^+ by [3.3.2] and [3.3.3]. Another reason for the low metal ion selectivity of large-size cryptands is their flexibility. Cox and co-workers have pointed out that cryptands with fewer than three oxygen atoms in the chains linking the bridgehead nitrogens are quite rigid and are able to discriminate more effectively between different cations [20]. Therefore, the degree of flexibility in large cryptands is high, resulting in low metal ion selectivity. In a recent review [1], Dietrich concluded that all cryptands studied so far showed generally poorer complexation and selectivity for two large cations, Rb^+ and Cs^+, than for the other cations of group 1.



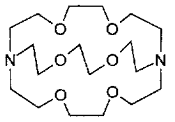
[1.1.1]



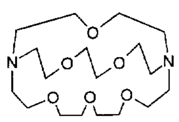
[2.1.1]



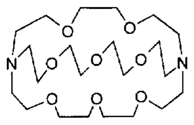
[2.2.1]



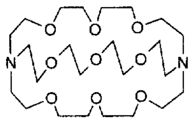
[2.2.2]



[3.2.1]



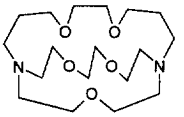
[3.3.2]



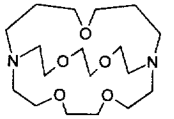
[3.3.3]

3. Symmetry of cryptands

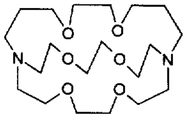
Symmetry is an important factor influencing the properties of cryptand complexation. Lukyanenko and co-workers have noted that the stability of the complexes of alkali and alkaline-earth metal ions depends considerably on cryptand symmetry [21]. They studied complexation properties of a series of propylene- and 2-hydroxypropylene-substituted cryptands (P_2[2.2.1], P_2[2.2.2], $(HP)_2$[2.2.2], etc.). As compared with cryptands [2.2.1] and [2.2.2], introduction of two propylene or 2-hydroxypropylene fragments results in a decrease in molecular symmetry. In most cases, these less symmetrical cryptands form less stable complexes with alkali and alkaline-earth metal ions (Table 2) than the corresponding cryptands [2.2.1] and [2.2.2]. The same effect has been also observed by Bradshaw and co-workers [22].



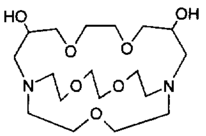
$P_2[2.2.1]$



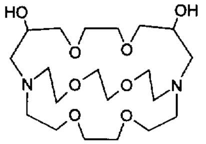
$P_2[1.2.2]$



$P_2[2.2.2]$



$(HP)_2[2.2.1]$



$(HP)_2[2.2.2]$

Effect of cryptand symmetry on metal ion selectivity has received little study. In Table 2, we see that high-symmetry [2.2.2] selects K^+ over Na^+ in 95/5 (v/v) methanol/water (95% MeOH) by a large factor ($\Delta \log K = \log K(K^+) - \log K(Na^+) = 2.54$, $K_{K^+}/K_{Na^+} = 347$). Although [2.2.1] selectively binds Na^+ over K^+, the selectivity factor is small ($\Delta \log K = 1.39$, $K_{Na^+}/K_{K^+} = 25$). The low Na^+/K^+ selectivity is related to the low symmetry of [2.2.1]. The propylene- and 2-hydroxypropylene-substituted cryptands show not only low binding constants but also low selectivities for alkali and alkaline-earth cations [21]. Propylene-substituted cryptands $P_2[2.2.1]$ and $P_2[1.2.2]$ selectively bind Na^+ over K^+ but by lower

Table 2

Log K values for the interactions of cryptands of different structures with metal ions[a] at 25 °C

	Li^+ (0.68)	Na^+ (0.95)	K^+ (1.33)	Rb^+ (1.48)	Cs^+ (1.69)	Mg^{2+} (0.66)	Ca^{2+} (0.99)	Sr^{2+} (1.13)	Ba^{2+} (1.35)
[2.2.1][b] (1.1)	4.18	8.84	7.45	5.80	3.90	<2	9.61	10.65	9.70
[2.2.2][b] (1.4)	1.8	7.21	9.75	8.40	3.54	<2	7.60	11.5	12
$P_2[2.2.1]$[c]	<2	4.83	4.14	3.12	<2	<2	4.36	4.33	4.92
$P_2[1.2.2]$[c]	<2	6.13	5.11	3.41	2.32	<2	5.20	5.81	5.05
$P_2[2.2.2]$[c]	<2	4.36	5.47	5.14	3.71	<2	3.74	4.81	7.53
$(HP)_2[2.2.1]$[c]	<2	3.07	2.44	<2	<2	4.32	5.63	5.72	5.51
$(HP)_2[2.2.2]$[c]	<2	5.75	5.13	4.31	<2	3.63	6.64	7.21	8.62
[3.2.1][d]	3.14	6.95	8.61	7.96	6.35	–	–	8.25	11.0
$M_2[2.2.2]$[e]	<2	5.5	2.42	<2	<2	–	–	–	–
$MP[2.2.2]$[f]	–	5.60	7.08	5.70	2.96	–	–	–	–
$(MP)_3[2.2.2]$[f]	<2	6.50	3.60	2.49	<2	–	–	–	–

[a] See footnote a of Table 1.

[b] Ref. [17]. Determined in 95/5 (v/v) methanol/water.

[c] Ref. [21]. Determined in 95/5 (v/v) methanol/water.

[d] Ref. [23]. Determined in 95/5 (v/v) methanol/water.

[e] Refs. [24,25]. Determined in 80/20 (v/v) methanol/water.

[f] Refs. [28,29]. Determined in 80/20 (v/v) methanol/water.

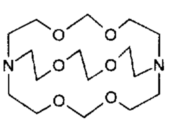
factors ($K_{Na^+}/K_{K^+}=5$ and 11, respectively) than [2.2.1] ($K_{Na^+}/K_{K^+}=25$). The 2-hydroxypropylene-substituted cryptand $(HP)_2$[2.2.1] exhibits the same low Na^+/K^+ selectivity as do P_2[2.2.1] and P_2[1.2.2] (Table 2). Compared with [2.2.2], P_2[2.2.2] shows a significantly lower K^+/Na^+ selectivity ($K_{K^+}/K_{Na^+}=13$) and $(HP)_2$[2.2.2] selects Na^+ over K^+ by only a small factor ($K_{Na^+}/K_{K^+}=4$).

Cryptand [3.2.1], a structural isomer of cryptand [2.2.2], displays much lower K^+/Na^+ selectivity ($K_{K^+}/K_{Na^+}=46$) than [2.2.2] in 95% MeOH (see Table 2). In addition, [3.2.1] forms less stable complexes with Na^+, K^+, Rb^+, Sr^{2+} and Ba^{2+} but more stable complexes with Li^+ and Cs^+ than cryptand [2.2.2]. It has been pointed out that the different complexation behavior of [3.2.1] from that of [2.2.2] is attributable to lower symmetry of [3.2.1] [23]. The high symmetry of [2.2.2] results in the electronegative oxygens being at a maximum separation in the coordination shell, presenting a more even charge distribution than that in the low-symmetrical [3.2.1]. A cryptand of high symmetry shows good selectivity for certain cations since it possesses a donor atom array with even distribution of the charges and the cavity radius of the cryptand matches only the cation whose ionic radius is close to that of the cavity. On the other hand, a low-symmetrical cryptand shows low selectivity for metal ions due to an uneven charge distribution.

The excellent cation binding and selectivity properties displayed by a high-symmetry cryptand can be understood as follows. Because the alkali and alkaline-earth metal ions are of spherical symmetry, they prefer a coordination environment having a spherical donor atom array. Therefore, high-symmetry cryptands usually show better complexation and selectivity properties than low-symmetry ones. A low-symmetry cryptand may produce a high strain energy when coordinated with a cation since the cryptand has to dispose its donor atoms close to a spherical-coordination array. Compared to [2.2.2] complexation with the same cations, the less favorable enthalpy changes for [3.2.1] complexation with Na^+, K^+, Rb^+, Sr^{2+} and Ba^{2+} (all have smaller $\log K$ values than the corresponding [2.2.2] complexes, see Table 2), but not with Cs^+, provide evidence that the [3.2.1] complexes had a larger steric strain than the [2.2.2] ones [23]. Thus, a rule to improve metal ion selectivity by cryptands is to use the best size-match ligand while keeping a highly symmetrical coordination array of the ligand.

From Table 1 we see that the radius of the spherical-symmetric [2.2.2] (1.4 Å) matches the ionic radius of K^+ (1.33 Å) and the cation is highly selected by [2.2.2]. The smaller [2.2.1] has Na^+/K^+ selectivity but the selectivity factor is not high for two reasons. First, the donor atom array of the ligand is not highly spherical symmetric. Second, the cavity radius of [2.2.1] (1.1 Å) does not match the ionic radius of Na^+ (0.95 Å) well. Therefore, a way to enhance the Na^+/K^+ selectivity is to reduce the size of the cryptand cavity and keep a highly symmetric coordination array.

A bismethylene-bridged cryptand, M_2[2.2.2], shows a significantly higher Na^+/K^+ selectivity ($K_{Na^+}/K_{K^+}=1200$ in 80/20 MeOH/water [24,25], see Table 2) as compared to [2.2.1]. The [2.2.2]-type donor atom array of M_2[2.2.2] maintains a high-symmetric coordination shell for the ligand and the two methylene units result in a decreased cavity radius to better match the ionic radius of Na^+. Therefore,

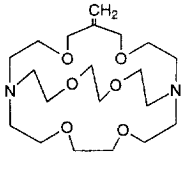


M_2[2.2.2]

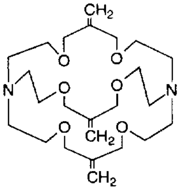
cryptand M_2[2.2.2] possesses both a high-symmetric donor atom array and the matched cavity size with Na^+ and greatly improves the selectivity for Na^+ over K^+.

4. Replacement of ethylene by propylene

The data in Table 2 show that the [2.2.2]-type cryptand $(HP)_2$[2.2.2] selects Na^+ ($\log K=5.75$) over K^+ ($\log K=5.13$), which is a reversal of the common K^+ over Na^+ selectivity order demonstrated by most [2.2.2]-type cryptands. This reversed K^+/Na^+ selectivity order is a result of replacement of ethylene by hydroxypropylene units. As the ethylene(s) of the cryptand bridge(s) are replaced by propylene(s), a large change in metal ion complexation can be observed. Since the propylene $CH_2CH_2CH_2$ is longer than the ethylene CH_2CH_2 group, one may expect that the cryptand cavity would be enlarged by incorporating the propylene unit(s) into the molecule and the resulting ligand(s) should selectively bind a larger cation. But actual complexation behavior is not as simple as expected. A propylene-containing cryptand usually has a tendency to bind small metal ions, which is a result of formation of six-membered chelate ring(s). The all-ethylene-containing cryptate complexes have only five-membered chelate rings. Incorporation of the propylene bridges into a cryptand results in cryptate complexes containing six-membered chelate rings. From an examination of binding constant data and molecular mechanics calculations, Hancock and Martell have concluded that large metal ions prefer five-membered chelate rings while small metal ions have a large preference for six-membered chelate rings [26,27]. Therefore, two six-membered chelate rings in the complexes of $(HP)_2$[2.2.2] favor complexation of the small-sized Na^+ over larger cations.



MP[2.2.2]



$(MP)_3$[2.2.2]

It has been demonstrated that incorporation of the 2-methylenepropylene group(s) into cryptand [2.2.2] (MP[2.2.2] and $(MP)_3$[2.2.2]) results in a large change in cation-binding properties [28]. The selectivity behavior of mono(2-methylenepropylene)-substituted MP[2.2.2] in 80/20 methanol/water is similar to that of [2.2.2] (see Fig. 1) but the difference between the log K values for the interactions of K^+ and Na^+ with MP[2.2.2] ($\Delta \log K = 1.48$, see Table 2) is much smaller than that with [2.2.2] ($\Delta \log K = 2.48$ [28]), indicating that a six-membered chelate ring in MP[2.2.2] increases small Na^+-binding and decreases large K^+-binding. As three 2-methylenepropylene groups are incorporated, the resulting $(MP)_3$[2.2.2] shows a very different complexation behavior from [2.2.2] (Fig. 1). Ligand $(MP)_3$[2.2.2] binds the small Na^+ more strongly than any of the other cations studied. The stability order $Na^+ \gg K^+ > Rb^+ > Cs^+$ is quite different from that of cryptand [2.2.2] and the Na^+/K^+ selectivity factor ($K_{Na^+}/K_{K^+} = 790$) is much higher than that by [2.2.1] ($K_{Na^+}/K_{K^+} = 25$).

Cryptand $(MP)_3$[2.2.2] possesses a high symmetry since the three methylenepropylene groups are introduced into its three bridges. This high-symmetric donor atom array of $(MP)_3$[2.2.2] is also an important factor for the high Na^+/K^+ selectivity. On the other hand, cryptand MP[2.2.2] is less symmetric than either [2.2.2] or $(MP)_3$[2.2.2] and MP[2.2.2] shows a low K^+/Na^+ selectivity. Therefore, a high selectivity for a small cation can be obtained when the cryptands are able to form a number of six-membered chelate rings (propylene derivatives on the bridges) with metal ions while the requirements of the high-symmetric donor atom array and size-matched cavity are met.

The substituents on the propylene chain have an effect on cation binding. If two unsubstituted propylene units are introduced into cryptand [2.2.2], such as P_2[2.2.2], the ligand still selects K^+ over Na^+ (Table 2). Therefore, the hydroxy (in $(HP)_2$[2.2.2]) and methylene (in $(MP)_3$[2.2.2]) substituents on the propylene units also play an important role in Na^+ over K^+ selectivity. The hydroxy and methylene groups may cause the cryptands to be in a proper conformation that selectively binds the small Na^+ [21,28]. In addition, attachment of electronegative hydroxyl and methylene groups to the propylene units decreases the basicity of the

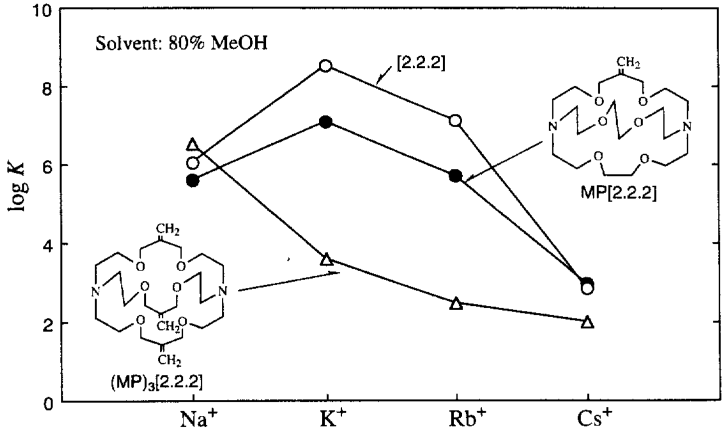
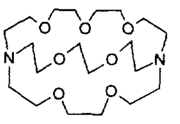
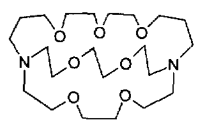


Fig. 1. Plots of log K vs the alkali cations for their interactions with cryptands [2.2.2] and 2-methylenepropylene-bridged cryptands MP[2.2.2] and $(MP)_3$[2.2.2]. (Taken from Ref. [28]).

adjacent oxygen and nitrogen atoms [21], resulting in a decrease in complex stability. This decrease in complex stability is probably more significant for large K^+ than for small Na^+ due to the different charge densities of the cations.



[3.2.2]



P_2[3.2.2]

It was shown that bispropylene-bridged cryptand P_2[3.2.2] displayed a different metal ion selectivity from cryptands [3.2.2] [22]. Cryptand P_2[3.2.2] selectively bound small Sr^{2+} ($\log K(H_2O) = 3.62$) over large Ba^{2+} ($\log K(H_2O) = 3.13$) [22] while [3.2.2] showed selectivity for Ba^{2+} ($\log K(H_2O) = 6.0$) over Sr^{2+} ($\log K(H_2O) = 3.4$) [17]. This reverse selectivity demonstrated by P_2[3.2.2] as compared with [3.2.2] was attributed to two six-membered chelate rings in the P_2[3.2.2] complexes [22].

5. Cryptands containing benzo and several other substituents

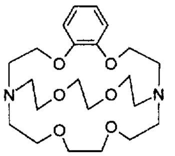
The effects of benzo and other substituents on the complexation properties of cryptands have been studied by several research groups [13,20,30–37]. Introduction of benzene rings into cryptands usually decreases metal ion binding and selectivity. As shown in Table 3, benzo- and dibenzo-substituted [2.2.2] (B[2.2.2] and B_2[2.2.2]) have lower binding constants for alkali and alkaline-earth metal ions than cryptand [2.2.2]. Cryptand [2.2.2] selectively binds K^+ over Na^+ in MeOH by 2.52 $\log K$ units, while B[2.2.2] and B_2[2.2.2] exhibit K^+/Na^+ selectivities of 1.71 and

Table 3
Log *K* values for the interactions of different cryptands with metal ions[a] in MeOH at 25 °C

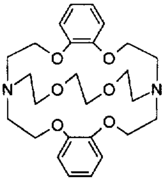
	Li^+ (0.68)	Na^+ (0.95)	K^+ (1.33)	Rb^+ (1.48)	Cs^+ (1.69)	Ca^{2+} (0.99)	Sr^{2+} (1.13)	Ba^{2+} (1.35)
[2.2.2] (1.4)	2.46[b]	7.97[b]	10.49[b]	9.10[b]	3.95[b]	8.16[d]	11.75[e]	12.89[c]
B[2.2.2]	2.19[f]	7.50[f]	9.21[f]	7.19[f]	2.99[f]	7.04[g]	10.32[g]	10.99[g]
B_2[2.2.2][h]	2.0	7.60	8.74	5.91	2.61	5.96[g]	8.83[g]	8.85[e]
C_2[2.2.2][g]	–	6.02	6.92	5.65	2.55	5.12	8.59	9.75
D[2.2.2][h]	2.0	7.0	9.42	7.61	3.21	–	–	–
L_2[2.2.2][i]	–[j]	–[j]	–[j]	–[j]	–[j]	3.58	4.01	2.90
1[k]	–[j]	4.03	4.66	4.31	3.94	–	3.72	4.01
2[k]	–[j]	3.76	4.58	3.92	2.90	–	–[j]	3.58
3[k]	–[j]	3.43	4.41	4.03	3.58	–	3.22	–[j]
4[k]	–[j]	3.67	5.10	4.68	3.72	–	3.80	4.03

[a] See footnote a of Table 1.
[b] Ref. [39]. [c] Ref. [41]. [d] Ref. [40]. [e] Ref. [33]. [f] Ref. [32]. [g] Ref. [36]. [h] Ref. [20] (except indicated).
[i] Ref. [35]. [j] Log *K* values cannot be determined accurately. [k] Ref. [37].

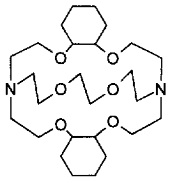
1.14 log *K* units, respectively. A series of chlorophenyl-containing cryptands (**1–4**) have been synthesized [38] and their complexation properties studied [37]. Data in Table 3 show that cryptands **1–4** form less stable complexes than not only cryptand [2.2.2] but also B[2.2.2] and B_2[2.2.2]. In addition, the K^+/Na^+ selectivity by ligands **1–4** (0.63–1.43 log *K* units) is significantly lower than that by ligand [2.2.2]. Tümmler and co-workers studied complexation properties of two pyridinophane cryptands (Py[2.2.1] and K_2Py[2.2.1]) [31]. They found that the thermodynamic stabilities of the Na^+ and K^+ complexes of Py[2.2.1] and K_2Py[2.2.1] in aqueous solution were similar to those of the corresponding complexes of [2.2.1] but the degree of selectivity was much less pronounced.



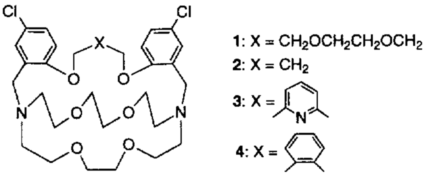
B[2.2.2]



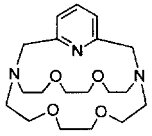
B_2[2.2.2]



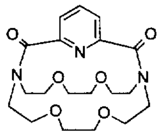
C_2[2.2.2]



1: X = $CH_2OCH_2CH_2OCH_2$
2: X = CH_2
3: X =
4: X =



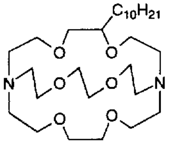
Py[2.2.1]



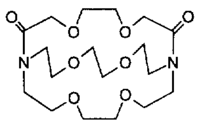
K_2Py[2.2.1]

It has been pointed out [20,33,36] that the effects of benzo substituents in cryptands are: (a) to diminish the cavity size, since the distance between the two oxygen atoms joined to the benzene ring is shorter than that in an unsubstituted chain; (b) to decrease the electron densities on these oxygen atoms; and (c) to reduce the flexibility of the ligand. All of these factors are responsible for low binding constants and K^+/Na^+ selectivity [20,33,36].

Several other substituents on the cryptands also reduce binding constants and metal ion selectivities. A dicyclohexano-substituted cryptand, C_2[2.2.2], has lower binding constants for alkali metal ions and lower K^+/Na^+ selectivity than even benzene-containing B[2.2.2] and B_2[2.2.2] (Table 3). Attachment of a long alkyl chain ($-C_{10}H_{21}$) to cryptand [2.2.2] to form D[2.2.2] results in the ligand (D[2.2.2]) that forms less stable complexes with alkali metal ions than [2.2.2] [20]. In this case, a very small decrease in K^+/Na^+ selectivity ($\Delta \log K = 2.42$) and an increase in K^+/Rb^+ selectivity ($\Delta \log K = 1.81$) are observed as compared with that found for the unsubstituted cryptand [2.2.2] ($\Delta \log K(\mathrm{K}^+/\mathrm{Na}^+) = 2.52$ and $\Delta \log K(\mathrm{K}^+/\mathrm{Rb}^+) = 1.39$, see Table 3). A drastic decrease in stability of the complexes of cryptand dilactam L_2[2.2.2] with alkali and alkaline-earth metal ions is shown in Table 3. No interactions can be detected in MeOH between L_2[2.2.2] and alkali metal ions. In acetonitrile, the binding constants of the L_2[2.2.2] with alkali and alkaline-earth metal ions were reduced by factors of 10^5–10^{10} compared with unsubstituted [2.2.2] [35]. The low binding abilities of dilactam cryptands were attributed to low basicity of the nitrogen atoms and increased rigidity of the ligands due to the carbonyl groups [35].



D[2.2.2]



L_2[2.2.2]

Cox and co-workers have shown that substituents on cryptands reduce the stability constants of the cryptate complexes by the cooperative action of reducing the formation rates and increasing the dissociation rates [20]. This change in rate constants is essentially a result of a decrease in molecular symmetry and flexibility of these cryptands due to attachment of the different groups onto the ligands. In order to form stable complexes, as mentioned in Section 3, the low-symmetric cryptands need to dispose their donor atoms close to a spherical-coordination array. This process causes a decreased formation constant. Similarly, increased rigidity in benzene-containing cryptands results in a slow complexation rate with metal ions. The increased dissociation rate is understandable since the low-symmetric cryptate complexes usually possess large steric strains.

Acknowledgements

The authors thank the Department of Energy, Office of Basic Energy Sciences for financial support through Grant No. DE-FG02-86ER 13463.

References

[1] B. Dietrich, in: G.W. Gokel (Ed.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, ch. 4, p. 153.
[2] B. Dietrich, J.-M. Lehn, J.-P. Sauvage, Tetrahedron Lett. 34 (1969) 2885.
[3] B. Dietrich, J.-M. Lehn, J.-P. Sauvage, Tetrahedron Lett. 34 (1969) 2889.
[4] B. Dietrich, P. Viout, J.-M. Lehn, Macrocyclic Chemistry, VCH, Weinheim, 1993.
[5] G.W. Gokel, Crown Ethers and Cryptands, The Royal Society of Chemistry, Cambridge, 1991.
[6] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 91 (1991) 1721.
[7] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 95 (1995) 2529.
[8] J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 27 (1988) 89.

[9] J.-M. Lehn, J. Inclusion Phenom. 6 (1988) 351.
[10] P.G. Potvin, J.-M. Lehn, in: R.M. Izatt, J.J. Christensen (Eds.), Synthesis of Macrocycles: the Design of Selective Complexing Agents, John Wiley and Sons, New York, 1987, p. 167.
[11] J.-M. Lehn, Science 227 (1985) 849.
[12] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, D. Sen, Chem. Rev. 85 (1985) 271.
[13] B. Dietrich, in: J.L. Atwood, J.E.D. Davies, D.P. MacNicol (Eds.), Inclusion Compounds, vol. 2, Academic Press, London, 1984, ch. 10, p. 337.
[14] D. Parker, Adv. Inorg. Chem. Radiochem. 27 (1983) 1.
[15] J.-M. Lehn, Acc. Chem. Res. 11 (1978) 49.
[16] J.-M. Lehn, Structure and Bonding 16 (1973) 1.
[17] J.-M. Lehn, J.P. Sauvage, J. Am. Chem. Soc. 97 (1975) 6700.
[18] H. Parham, M. Shamsipur, Polyhedron 11 (1992) 987.
[19] M.H. Abraham, A.F.D. de Namor, R.A. Schulz, J. Chem. Soc., Faraday Trans. I 76 (1980) 869.
[20] B.G. Cox, P. Firman, I. Schneider, H. Schneider, Inorg. Chim. Acta 49 (1981) 153.
[21] N.G. Lukyanenko, N.Y. Nazarova, V.I. Vetrogon, N.I. Vetrogon, A.S. Reder, Polyhedron 9 (1990) 1369.
[22] K.E. Krakowiak, J.S. Bradshaw, N.K. Dalley, C.-Y. Zhu, G.-L. Yi, J.C. Curtis, D. Li, R.M. Izatt, J. Org. Chem. 57 (1992) 3166.
[23] X.X. Zhang, R.M. Izatt, K.E. Krakowiak, J.S. Bradshaw, Inorg. Chim. Acta 254 (1997) 43.
[24] J.S. Bradshaw, H.-Y. An, K.E. Krakowiak, T.-M. Wang, C.-Y. Zhu, R.M. Izatt, J. Org. Chem. 57 (1992) 6112.
[25] J.S. Bradshaw, K.E. Krakowiak, H.-Y. An, T.-M. Wang, C.-Y. Zhu, R.M. Izatt, Tetrahedron Lett. 33 (1992) 4871.
[26] R.D. Hancock, A.E. Martell, Chem. Rev. 89 (1989) 1875.
[27] R.D. Hancock, Pure Appl. Chem. 58 (1986) 1445.
[28] K.E. Krakowiak, X.X. Zhang, J.S. Bradshaw, C.Y. Zhu, R.M. Izatt, J. Inclusion Phenom. 23 (1995) 223.
[29] X.X. Zhang, A.V. Bordunov, R.M. Izatt, J.S. Bradshaw, in: L. Echegoyen, A.E. Kaifer (Eds.), Physical Supramolecular Chemistry, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, 1996, p. 413.
[30] B. Dietrich, J.M. Lehn, J.P. Sauvage, J. Chem. Soc., Chem. Commun. (1973) 15.
[31] B. Tümmler, G. Maass, E. Weber, W. Wehner, F. Vögtle, J. Am. Chem. Soc. 99 (1977) 4683.
[32] B.G. Cox, D. Knop, H. Schneider, J. Phys. Chem. 84 (1980) 320.
[33] B.G. Cox, Ng. Van Truong, J. Garcia-Rosas, H. Schneider, J. Phys. Chem. 88 (1984) 996.
[34] M.K. Chantooni Jr., I.M. Kolthoff, J. Solution Chem. 14 (1985) 1.
[35] H.-J. Buschmann, Inorg. Chim. Acta 120 (1986) 125.
[36] H.-J. Buschmann, Inorg. Chim. Acta 134 (1987) 225.
[37] X.X. Zhang, J.S. Bradshaw, A.V. Bordunov, V.N. Pastushok, R.M. Izatt, Inorg. Chim. Acta, to be published.
[38] A.V. Bordunov, N.K. Dalley, X. Kou, J.S. Bradshaw, V.N. Pastushok, J. Heterocyclic Chem. 33 (1996) 933.
[39] H.-J. Buschmann, Inorg. Chim. Acta 125 (1986) 31.
[40] H.-J. Buschmann, J. Solution Chem. 15 (1986) 453.
[41] F. Arnaud-Neu, R. Yahya, M.J. Schwing-Weill, J. Chim. Phys. Phys.-Chim. Biol. 83 (1986) 403.