Coordination Chemistry Reviews, 87 (1988) 55–213
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPREHENSIVE COORDINATION CHEMISTRY OF ALKALI AND ALKALINE EARTH CATIONS WITH MACROCYCLIC MULTIDENTATES: LATEST POSITION

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(Received 27 March 1986)

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0010-8545/88/$55.30

KEY TO NOTATIONS

The electrically neutral compounds (including solvents and crowns) have been denoted by capital letters while the anions use lower-case letters; the crown-related macrocycles have been denoted by Roman numerals (**I–CXLV**). An alkyl group present in a crown has been written prior to an aryl moiety when the latter carries the former, otherwise the aryl moiety precedes the alkyl group(s); in DBTM18C6, for example, the four methyl groups are carried by the ring carbons while in MB15C5 the benzo group carries the methyl group. A comprehensive list of notations follows.

AC	acetone
ans^-	8-anilino-1-naphthalene sulphonate
asym-DB24C8	asymmetric dibenzo-24-crown-8
B13C4	benzo-13-crown-4
B15C5	benzo-15-crown-5
B18C6	benzo-18-crown-6
BB15C5	*t*-butylbenzo-15-crown-5
BDM15C5	benzodimethyl-15-crown-5
12C4	12-crown-4
15C5	15-crown-5
16C4	16-crown-4
18C6	18-crown-6

21C7	21-crown-7
24C8	24-crown-8
C15C5	cyclohexano-15-crown-5
C18C6	cyclohexano-18-crown-6
DB14C4	dibenzo-14-crown-4
DB15C5	dibenzo-15-crown-5
DB18C5	dibenzo-18-crown-5
DB18C6	dibenzo-18-crown-6
DB21C7	dibenzo-21-crown-7
DB24C8	dibenzo-24-crown-8
DB27C9	dibenzo-27-crown-9
DB30C10	dibenzo-30-crown-10
DBDB18C6	di-*t*-butyldibenzo-18-crown-6
DBDM15C5	dibenzodimethyl-15-crown-5
DBDM18C6	dibenzodimethyl-18-crown-6
DBTM18C6	dibenzotetramethyl-18-crown-6
DC14C4	dicyclohexano-14-crown-4
DC18C6	dicyclohexano-18-crown-6
DC21C7	dicyclohexano-21-crown-7
DC24C8	dicyclohexano-24-crown-8
DC30C10	dicyclohexano-30-crown-10
DCE	dichloroethane
DM18C6	dimethyl-18-crown-6
DMDB18C6	dimethyldibenzo-18-crown-6
DMDB24C8	dimethyldibenzo-24-crown-8
DMDB30C10	dimethyldibenzo-30-crown-10
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulphoxide
dnb^-	3,5-dinitrobenzoate
dnp^-	2,4-dinitrophenolate
eaa^-	ethylacetoacetato
fl^-	fluorenyl
GDN	Gutmann donor number
L^-	an organic anion
M^+	an alkali cation
M^{2+}	an alkaline earth cation
M^{z+}	general abbreviation for M^+ and M^{2+}
MB15C5	methylbenzo-15-crown-5
MB18C6	methylbenzo-18-crown-6
MCM	general abbreviation for a macrocyclic multidentate
MeCN	acetonitrile

N20C6	naphtho-20-crown-6
NM	nitromethane
onp^-	*o*-nitrophenolate
PC	propylene carbonate
pic^-	picrate (2,4,6-trinitrophenolate)
sal^-	salicylate
$salen^-$	*N*, *N*′-ethylenebis(salicylideneaminato)
TBDB18C6	tetra-*t*-butyldibenzo-18-crown-6
TC18C6	tetracyclohexyl-18-crown-6
$tcne^-$	tetracyanoethylene radical anion
$tcnq^-$	tetracyanoquinodimethane radical anion
TCNQ	tetracyanoquinodimethane (neutral molecule)
THF	tetrahydrofuran
TM12C4	tetramethyl-12-crown-4
TM18C6	tetramethyl-18-crown-6
tos^-	tosylate
TP18C6	tetraphenyl-18-crown-6
X^-	an inorganic anion

A. INTRODUCTION

Alkali (M^+) and alkaline earth (M^{2+}) cations (general abbreviation M^{z+}) play diverse vital roles [1–4] in biological systems. The mysterious chemical diversity of the seemingly alike cations (Na^+ and K^+, and Mg^{2+} and Ca^{2+}), especially with respect to their membrane transport phenomena [5–8], has attracted much attention and has been a challenge to the biochemist and to the inorganic chemist.

Unfortunately, until recently, little was known about the principles of interaction of M^{z+} especially with respect to neutral ligands so that the inorganic chemist has not been able to contribute much to the understanding of and the control of the role of M^{z+} in nature. Worthwhile studies could not be carried out because of the spherical and hard nature of these cations and their lack of convenient magnetic and spectroscopic properties; even their analytical chemistry has been only weakly based. Interactivity of M^{z+} with conventional bidentate, tridentate or even polydentate ligands has been detected or postulated since the beginning of this century [9] but the interactive principles of these cations could not be delineated because of their unfavourable or weak complexation with such molecules. The principles of interaction discovered through study of transition metal cations were presumed to apply to the chemistry of M^{z+} and this presumption constantly hampered the development of the subject.

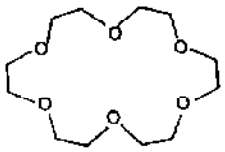


Fig. 1. A typical cyclic polyether (crown ether).

In 1967, a golden year in the context of the present subject, Pedersen [10] at Delaware discovered that M^{z+} undergo complexation with the macrocyclic polyethers (crown ethers) to produce well-defined crystalline products. This work was soon extended to the synthesis and study of a wide variety of M^{z+} complexes with these macrocycles. Because of the important biological implications of Na^+, K^+, Mg^{2+} and Ca^{2+}, there was great interest in understanding the properties of M^{z+} bound to crown ethers (Fig. 1).

The solid state studies (X-ray diffraction) and solution studies (calorimetric, electrometric and spectrometric) on crown ether M^{z+} complexes have expanded our understanding of the bonding behaviour of M^{z+} towards neutral ligands vis-a-vis anionic species including solvents [11]. Since 1975, theoretical approaches have also been adopted to understand M^{z+}–crown interaction.

Various crown-related macrocycles incorporating donor atoms other than oxygen have been synthesized [12–21] and their interaction with M^{z+} investigated in solution as well as in the solid state; a number of such macrocycles reveal a better binding ability than crowns. This work started soon after Pedersen's original discovery, but interest has grown rapidly within the last few years. This could partly be due to an attempt to understand the complexing characteristics of, for example, the naturally occurring antibiotics which became popular in the late sixties.

From 1969 onwards, Lehn's school in Strasbourg gave a new dimension to the structural features of the cyclic multidentates by introducing bicyclic [22], tricyclic [23] and polycyclic [24] molecules, known as cryptands, reviewed in refs. 25–28. The chelating potential of these ligands for M^{z+} can be assessed in view of the observation that a bicyclic cryptand, for example, is able to render $BaSO_4$ soluble in water. X-ray analysis of solid M^{z+}–cryptand complexes (cryptates) has revealed that a cryptand can swallow the cation to produce, in general, an inclusion type of complex. Solution studies have shown that seemingly alike pairs of cations can be discriminated through control of the cavity size of the cryptand and through variation of the nature of substituents on its exterior.

Around the same time, Simon's school in Zurich planned [29] the synthesis and study of acyclic macromolecular ligands for selective complexation and determination of M^{z+}, essentially through their use as ionophores

located within membranes. These researchers have illustrated [30] that a high specificity of complexation can be achieved through molecular tailoring and through a variation in the nature of the study medium. Studies on other acyclic multidentates such as poly(oxyethylene) derivatives [31,32] have also been carried out with M^{z+}.

Moore and Pressman [33] in Philadelphia made a pioneering observation that valinomycin, a cyclic depsipeptide antibiotic, is capable of stimulating the transport of K^+ across the rat mitochondrial membrane. The significance (and promise) of this observation was appreciated, particularly in the late sixties, when interesting results with various synthetic multidentates also started becoming available. This aroused continuing interest in the study of the diverse cyclic and acyclic multidentates of natural [34–39] and synthetic origin.

Research on synthetic macrocyclic multidentates (general abbreviation, MCM) soon became oriented in different directions which included complexation studies of M^{z+} with multidentates using M^{z+} as controlling tools, kinetic studies on M^{z+}–multidentate complexation, stability measurements with respect to M^{z+}–MCM in solution, diffraction studies in the solid state, template use of M^{z+} during synthesis of especially the cyclic multidentates and M^{z+} stabilization for the purpose of anion activation in organic synthesis. This has led to the publication of various reviews [9,11,17,20,21,31,40–65]. The macrocyclic effect [66,67], upon which the complexation strength of MCM with inorganic cations depends, is under continued investigation [68–74].

In this review we attempt a critical discussion of M^{z+} complexation involving synthetic MCM while highlighting in particular the coordinative contributions of the M^{z+} therein. Whereas a discussion of coordination compounds of transition metal cations is usually cation oriented, discussion of M^{z+}–MCM must also involve substantial description of the MCM. In this article, we have primarily discussed those MCM which have provided useful information about cation coordination.

The attention of the reader is drawn in particular to the results with the newly developed MCM and to the results of extraction and transport—the phenomena which are apparently relevant to membrane transport in natural systems. Mere compilation of data and repetitive discussion on similar systems have been avoided while discussion has mainly been focused on those systems which have aided consolidation of the knowledge with regard to the chemistry of M^{z+}; for exhaustive thermodynamic and kinetic data reference may be made to Izatt et al. [691].

The literature to the end of 1983 has been reviewed in the main text while a compact and up-to-date account of the developments between 1984 and 1986 has been presented in Section D. This section has been consciously

separated from the main text not only to single out the latest trends but more so to enable the reader to form an idea that earlier conclusions about reaction trends and the chemical principles are confirmed through later work. Emphasis has been laid on the results published within the last 8 years. Necessary earlier information has also been included. All theoretical attempts to understand the M^{z+}–MCM interaction have been included. Such a description of the subject should help a broad correlation of the in vitro and in vivo systems, and that of the solid state chemistry with the chemistry in solution.

B. CROWNS

Cyclic polyethers (crown ethers or simply crowns) are the first MCM to be used as ligands for M^{z+} and continue to be highly useful in this regard. The basic part of a crown is the donor ring which is usually constituted of the repeating $-OCH_2CH_2-$ units as shown in Fig. 1. Pedersen [10] devised a trivial nomenclature for these compounds which is still being followed; see, however, Weber and Vögtle [75] for an alternative nomenclature ("coronands"). The notations shown in Fig. 2 are convenient and expressive with respect to the broad structural aspects of the molecule. The synthetic strategies for these compounds have been reviewed [14,18–20].

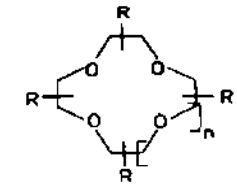
The complexing ability and hence molecular flexibility is determined basically by its ring size (the oxygen atoms contained in it) and the nature of the substituted moieties carried by it. The M^{z+}–crown interaction originates from an ion–dipole type of interaction between M^{z+} and the donor oxygens; the resulting complex (encapsulate) is usually crystalline.

The work with crowns (Fig. 2) has been executed essentially from the following viewpoints: (i) synthesis of M^{z+}(anion)(crown) complexes under a variety of conditions and X-ray analysis of these systems with a view to determining the bonding modes of M^{z+} as well as the conformational and stereochemical aspects of the crown molecule(s) [32,41,49,76]; (ii) determination of equilibrium [9,52,691] and rate [50,52,691] constants for diverse M^{z+}–crown systems in different media; (iii) phase-transfer studies of M^{z+} under the effect of a crown using two-phase extraction [62,77] or three-phase transport [56,61] systems; (iv) theoretical investigation [78–82] to determine the nature of bonding. The crowns have also been used extensively to complex M^{z+} for the purpose of activation of the counter-anion (for use as efficient nucleophiles in organic reactions [48,58]) as well as for generation of alkali anions [83,84].

(i) M^{z+}–crown solid complexes—general

For M^+, the synthesis of complexes with crowns is possible with inorganic (X^-) as well as organic (L^-) counter-anions [10,85–105]. However, in the

case of M^{2+}, for which the cation–anion involvements are stronger and the salts are relatively less soluble, the salts of the rather charge-delocalized anions are complexed. Such anions include thiocyanate (NCS^-) [10,85,96,101,102,106–110], perchlorate (ClO_4^-) [95,108,111,112], tetraphenylborate (BPh_4^-) [108,113], 3,5-dinitrobenzoate (dnb^-) [114,115], nitrophenolate, picrate (pic^-) or 2,4-dinitrophenolate (dnp^-) [95,116–121], salicylate (sal^-) [117,119], tosylate (tos^-) [88], fluorenyl (fl^-) [122] and the tetracyanoquinodimethane radical anion ($tcnq^-$) [100,123]. The use of an ionizing (protic polar) medium [124,125] is especially necessary for the highly M^{z+} bound anions such as halide; under these conditions, complex formation is possible for a potential and not-so-large cavity crown such as 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6) and benzo-18-crown-6 (B18C6). We are rather intrigued as to why tos^-, with which investigations were reported in the early seventies [88,126], has not become a popular anion for studies on the higher charge



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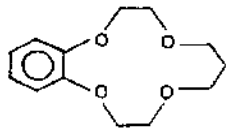

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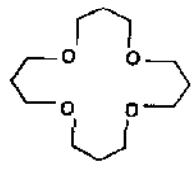

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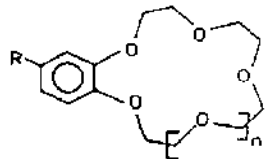

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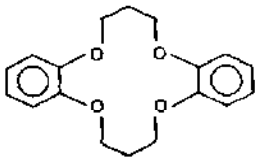

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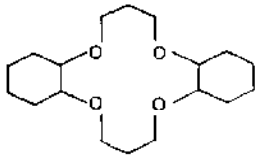

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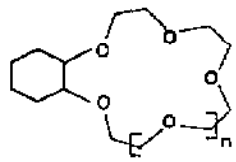

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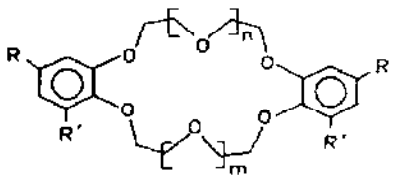

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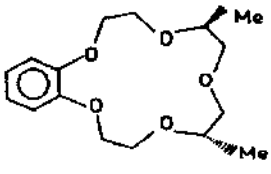

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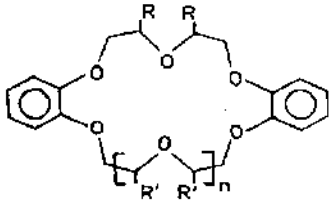

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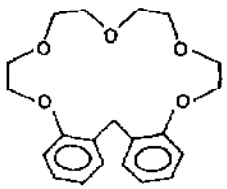

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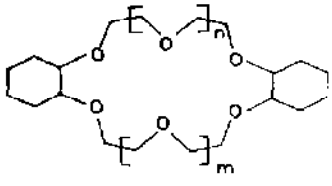

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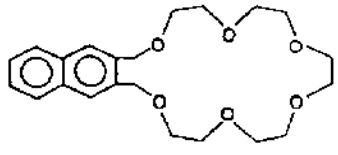

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density cations. Crown complexes of M^{z+}–carbanion salts have been reported from time to time [98–100,104,122,123]. M^{z+} complexes containing $tcnq^-$, known first in 1979, are attracting increasing attention [99,100,123,127].

For the synthesis of a complex the presence of a particular solvating (cation–anion pair loosening) solvent such as water is sometimes indispensable. This was first noted by one of us with regard to the synthesis of the complex [Na(B15C5)(H_2O)]I from a 1 : 1 ethanolic solution of NaI and B15C5 [91]. Analogous anhydrous or even the alcohol-solvated complex could not be synthesized through the use of dry methanol or ethanol; only the hydrated product can be crystallized for which it is, of course, essential to provide the necessary aqueous content to the system. Water is required to satisfy the coordinative characteristics of Na^+ in the lattice and, through its co-interaction, the water molecule not only causes the ion pair loosening of the original salt (and thereby makes the cation available to the crown molecule) but also holds the anion permanently separated from the cation (as revealed by the structural analysis of the complex [Na(B15C5)(H_2O)]I [128]). The role of water is further discussed with regard to Ca(pic)$_2$–B15C5 systems (see Section B (iii) (b)).

Fig. 2. The crown molecules discussed in the text: (i) R = H, n = 1: 12-crown-4 (12C4); (ii) R = H, n = 2: 15-crown-5 (15C5); (iii) R = H, n = 3: 18-crown-6 (18C6); (iv) R = H, n = 4: 21-crown-7 (21C7); (v) R = H, n = 5: 24-crown-8 (24C8); (vi) R = Me, n = 1: tetramethyl-12-crown-4 (TM12C4); (vii) benzo-13-crown-4 (B13C4); (viii) dibenzo-14-crown-4 (DB14C4); (ix) dicyclohexano-14-crown-4 (DC14C4); (x) 16-crown-4 (16C4); (xi) R = H, n = 1: benzo-15-crown-5 (B15C5); (xii) R = H, n = 2: benzo-18-crown-6 (B18C6); (xiii) R = Me, n = 1: methylbenzo-15-crown-5 (MB15C5); (xiv) R = Me, n = 2: methylbenzo-18-crown-6 (MB18C6); (xv) R = *t*-Bu, n = 1: *t*-butylbenzo-15-crown-5 (BB15C5); (xvi) n = 1: cyclohexano-15-crown-5 (C15C5); (xvii) n = 2: cyclohexano-18-crown-6 (C18C6); (xviii) R = R′ = H, n = 0, m = 1: dibenzo-15-crown-5 (DB15C5); (xix) R = R′ = H, n = m = 1: dibenzo-18-crown-6 (DB18C6); (xx) R = R′ = H, n = 1, m = 2: dibenzo-21-crown-7 (DB21C7); (xxi) R = R′ = H, n = m = 2: dibenzo-24-crown-8 (DB24C8); (xxii) R = R′ = H, n = 2, m = 3: dibenzo-27-crown-9 (DB27C9); (xxiii) R = R′ = H, n = m = 3: dibenzo-30-crown-10 (DB30C10); (xxiv) R = R′ = H, n = 1, m = 3: asymmetric dibenzo-24-crown-8 (*asym*-DB24C8); (xxv) R = Me, R′ = H, n = m = 1: dimethyldibenzo-18-crown-6 (DMDB18C6); (xxvi) R = Me, R′ = H, n = m = 2: dimethyldibenzo-24-crown-8 (DMDB24C8); (xxvii) R = Me, R′ = H, n = m = 3: dimethyldibenzo-30-crown-10 (DMDB30C10); (xxviii) R = *t*-Bu, R′ = H, n = m = 1: di-*t*-butyldibenzo-18-crown-6 (DBDB18C6); (xxix) R = R′ = *t*-Bu, n = m = 1: tetra-*t*-butyldibenzo-18-crown-6 (TBDB18C6); (xxx) benzodimethyl-15-crown-5 (BDM15C5); (xxxi) R = Me, R′ = H, n = 0; dibenzodimethyl-15-crown-5 (DBDM15C5); (xxxii) R = Me, R′ = H, n = 1; dibenzodimethyl-18-crown-6 (DBDM18C6); (xxxiii) R = R′ = Me, n = 1: dibenzotetramethyl-18-crown-6 (DBTM18C6); (xxxiv) dibenzo-18-crown-5 (DB18C5); (xxxv) n = m = 1: dicyclohexano-18-crown-6 (DC18C6); (xxxvi) n = 1, m = 2: dicyclohexano-21-crown-7 (DC21C7); (xxxvii) n = m = 2: dicyclohexano-24-crown-8 (DC24C8); (xxxviii) naphtho-20-crown-6 (N20C6).

(ii) M^{z+}–crown interaction modes in solid complexes

A coordination chemist should be mainly interested in examining the ligandphilicity of the cation as against its "anionphilicity" towards the charge neutralizer(s) and the solvating molecule(s) and, consequently, in the stereochemical location of the neutral ligands (vis-a-vis the anionic species) with respect to the cation. Along these lines we examine herein the interactive aspects of M^{z+} for the various well-characterized M^{z+}–crown systems.

Figure 3 schematically displays the diverse types of crown/anion preferences noted for different M^{z+} in the crystal lattice known from X-ray diffraction techniques. Table 1 indexes important structural information for recently studied M^{z+}–crown systems. The structural features are not without chemical significance. They are in fact helpful for revealing the Lewis acid status of the cations concerned and also the crown/anion preferences under the diverse conditions which are ultimately to be related to the reasons linked to the chemical diversities of the cations in the biological systems. This chemical significance may not be derived if the structural information is examined, for instance, simply from the viewpoint of the cation with

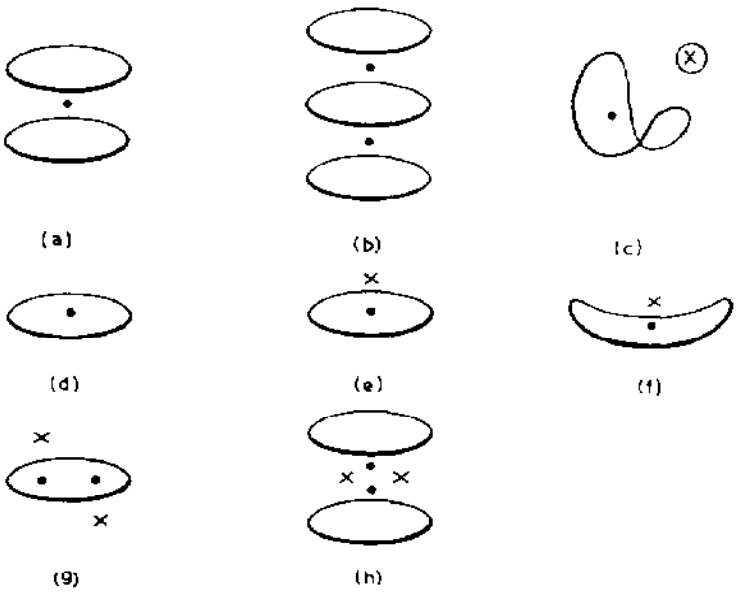


Fig. 3. A schematic representation of the different M^{z+}–crown systems displaying various crown/anion preferences: (a) 1 : 2 sandwich encapsulate; (b) 2 : 3 club-sandwich encapsulate; (c) 1 : 1 wrap-around encapsulate; (d) 1 : 1 cation–cavity compatible anion-separated encapsulate; (e) 1 : 1 anion-paired encapsulate wherein cation-cavity is comparable; (f) 1 : 1 anion-paired encapsulate wherein cavity size exceeds cation size; (g) bimetallic 2 : 1 anion-paired encapsulate; (h) dimeric, viz. 2 : 2 anion-paired encapsulate.

TABLE 1

Crystallographic description of recently studied solid M^{z+}–crown complexes [a]

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
LiNCS(12C4)	Li^+–O 2.05–2.14 Li^+–N 1.96	5	161
LiNCS(B13C4)	Li^+–O 2.01–2.16 Li^+–N 1.95	5 (distorted between square pyramid and trigonal bipyramid)	162
LiNCS(DB14C4)	Li^+–O 2.03–2.05 Li^+–N 1.96	5 (square pyramid)	164
LiNCS(16C4)	Li^+–O 2.07–2.09 Li^+–N 2.04	5	165
[Li(pic)$(H_2O)_2$]B15C5	Li^+–OH_2 1.86, 1.87 Li^+–O^- 1.92 Li^+–O(*o*-NO_2) 2.04	4 (tetrahedron)	188
[Li(18C6)$(H_2O)_2$]ClO_4	Li^+–O 2.07, 2.12 Li^+–OH_2 1.91, 1.92	4	151
$(LiNCS)_2$(18C6)·$2H_2O$	Li^+(1)–O 1.99, 2.07 Li^+(1)–OH_2 1.90, 1.97 Li^+(2)–O 1.99 Li^+(2)–OH_2 2.00 Li^+(2)–N 2.00, 2.01	4 4	151
[Na(12C4)$_2$]ClO_4	Na^+–O 2.47–2.54	8 (slightly distorted rectangular antiprism)	136
NaNCS(15C5)·$\frac{1}{2}H_2O$			166
A: [NaNCS(15C5)]	Na^+–O 2.35–2.50 Na^+–N 2.48	6	
B: [NaNCS(15C5)(H_2O)]	Na^+–O 2.33–2.51 Na^+–OH_2 2.48 Na^+–N 2.26	7	
Na(eaa)(15C5)	Na^+–O 2.42–2.56 Na^+–O(enolate) 2.30, 2.32	7	167
$NaClO_4$(B15C5)	Na^+–O 2.37–2.46 Na^+–O^- 2.43, 2.63	7	138
[Na(B15C5)$_2$]ClO_4	Na^+–O 2.63–2.94	4 [b]	138
[Na(B15C5)$_2$]BPh_4	Na^+–O 2.48–3.30	5 [c]	138
Na(pic)(B15C5)	Na^+–O 2.40–2.50 Na^+–O^- 2.35 Na^+–O(*o*-NO_2) 2.51	7	168
[Na(dnb)(B15C5)]H_2O	Na^+–O 2.41–2.56 Na^+–O^- 2.45	6	169
Na_2(tetrachlorodioxo-uranate)(B15C5)$_2$	Na^+–O^- 2.40–2.57 Na^+–Cl^- 2.82, 2.95	7	184
NaNCS(DB18C5)	Na^+–O 2.37–2.55 Na^+–N 2.34	6 (pentagonal pyramid)	170

TABLE 1 (continued)

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
$Na(P(CN)_2)(18C6)\cdot THF$			159
A: $[Na(18C6)(THF)_2]^+$	Na^+–O 2.71–2.79 Na^+–O(THF) av. 2.36	8 (hexagonal bipyramid)	
B: $[Na(P(CN)_2)_2(18C6)]^-$	Na^+–O 2.73–2.78 Na^+–N 2.44, 2.48	8 (hexagonal bipyramid)	
$[Na(18C6)(THF)_2]_2$ $[P_2(CN)_6X_2](X = Br$ or I)	Na^+–O not mentioned	8	160
$Na(W(CO)_5(SH))(18C6)$	Na^+–O 2.62–2.91 Na^+–O(CO) 2.41 Na^+–S 3.01	8 (slightly distorted hexagonal bipyramid)	171
$Na(W_2(CO)_{10}(\mu\text{-}SH))(18C6)$	Na^+–O 2.58–2.73 Na^+–O(CO) 2.43, 2.47	8 (very distorted hexagonal bipyramid)	171
$(Co(salen)Na)_2$ (DC18C6 *cis–anti–cis*)	Na^+–O 2.43–2.58 Na^+–O(salen) 2.26, 2.34	5 (irregular)	180
[Na(*asym*-DB24C8)]ClO_4	Na^+–O 2.45–2.72	8 (distorted square antiprism)	150
$(NaNCS)_2$(DB30C10)	Na^+–O 2.40–2.49 Na^+–O(bridge) 2.53, 2.59 Na^+–N 2.36	7 (approx. pentagonal bipyramid)	176
$[K(B15C5)_2]$pic	K^+–O 2.81–3.00	10	130
$[K(B15C5)_2](dnb\cdot 2Hdnb)$	K^+–O 2.76–3.10	10	131
K_2(phthalocyanine)$(18C6)_2$ $\cdot 1.5C_6H_6$	K^+–O av. 3.39 K^+–N av. 2.91	10	185
$K_2(Mo_6O_{19})(18C6)_2\cdot H_2O$	K^+(1)–O 2.77–2.88 K^+(1)–OH_2 2.89 K^+(1)–O(anion) 2.70 K^+(2)–O 2.72–2.88 K^+(2)–OH_2 2.93 K^+(2)–O(anion) 2.72	8 (hexagonal bipyramid)	186
$K_2MoO_4(18C6)_2\cdot 5H_2O$			187
A: $[K(18C6)(H_2O)_2]^+$	K^+(1)–O 2.78–3.05 K^+(1)–OH_2 2.78, 2.82	8	
B: $[KMoO_4(18C6)(H_2O)]^-$	K^+(2)–O 2.76–2.99 K^+(2)–OH_2 2.81 K^+(2)–O(anion) 2.79	8	
KI(DB18C6)·thiourea	K^+–O 2.71–2.80 K^+–I^- 3.57	7 (hexagonal pyramid)	173
$K(Al_2Me_6Cl)$(DB18C6) $\cdot 2C_6H_6$[d]	K^+–O 2.71–2.76	not mentioned	174
[K(DB30C10)]NCS	K^+–O 2.83–2.96	10	148

TABLE 1 (continued)

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
$[Rb(DB30C10)]NCS \cdot H_2O$	Rb^+–O 2.96–3.19	10	149
$NaK(sal)_2(DB24C8)$	Na^+–O 2.54–2.65	6	669
	Na^+–O^- 2.31–2.56		
	K^+–O 2.68–2.91	7	
	K^+–O^- 2.47–2.71		
Cs(pic)(B15C5) [e]	Cs^+–O 3.00–3.24	9	144
	Cs^+–O^- 3.03		
	Cs^+–O(*o*-NO_2) 3.01		
	Cs^+–O(*p*-NO_2) 3.17, 3.42		
$[Cs_9(18C6)_{14}]^{9+}$ $[Rh_{22}(CO)_{35}H_x]^{5-}$ $[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$			139
A: $[Cs(18C6)CO]^+$	Cs^+–O 3.09–3.69	8	
	Cs^+–O(CO) av. 3.51		
B: $[Cs(18C6)_2]^+$ [f]	Cs^+ (1)–O 3.25–3.74	12 (hexagonal antiprism)	
	Cs^+ (2)–O 3.64–3.84	12 (hexagonal antiprism)	
C: $[Cs_2(18C6)_3]^{2+}$ [g]	Cs^+–O 3.29–4.32	12 (hexagonal prism)	
$[Ba(15C5)_2](Br_2,2H_2O)$	Ba^{2+}–O 2.75–2.88	10 (pentagonal antiprism)	125
$Ba(pic)_2(B15C5) \cdot H_2O$ [h]	Ba^{2+}–O 2.80–3.00	10	121
	Ba^{2+}–OH_2 2.71		
	Ba^{2+}–O^- 2.64, 2.67		
	Ba^{2+}–O(*o*-NO_2) 2.83, 2.99		
$[Ba(dnb)_2(B15C5)]_2$	Ba^{2+}–O 2.89–3.09	9	115
	Ba^{2+}–O^- 2.64–2.69		

[a] For a description of the earlier M^{z+}–crown complexes see ref. 9.

[b] There are only four contacts of length less than 2.7 Å.

[c] There are only five contacts of length less than 2.7 Å; the bonding pattern of this encapsulate is different from that of the preceding encapsulate.

[d] Association of K^+ with the aromatic π cloud as well as a methyl group of the Al_2Me_6Cl anion is present.

[e] The complex Rb(pic)(B15C5) [145] is isomorphous.

[f] There are two types of sandwiches, one of which shows greater disparity in the bond distances.

[g] The breakdown of this wide range of bond distances (Å) is as follows: Cs^+ (1)–O(crown A) av. 3.59, range 3.51–3.67; Cs^+ (1)–O(crown B) av. 3.79, range 3.29–4.25; Cs^+ (2)–O(crown B) av. 3.69, range 3.35–3.96; Cs^+ (2)–O(crown C) av. 4.03, range 3.76–4.32.

[h] The complex $Sr(pic)_2(B15C5) \cdot H_2O$ is isomorphous [120].

respect to that of the donor ring [49] but it does ensue when the factors related to the crown/anion preferences of a cation are sought as in the following categorization.

(a) Charge-separated encapsulates

Such an encapsulate can be (i) a 1 : 2 sandwich encapsulate involving two small cavity crown molecules, (ii) a 2 : 3 club sandwich encapsulate involving three molecules of the crown for two cations, or (iii) a 1 : 1 wrap-around encapsulate involving a large cavity crown. Herein the cation does not interact with the anionic species but is exclusively coordinated to the crown oxygens.

The sandwich encapsulates (Fig. 3(a)) are ordinarily formed when (i) a "large" (low charge density) monovalent cation such as K^+, Rb^+ or Cs^+ is complexed [129–133] with a small cavity crown such as B15C5, and (ii) a higher charge density M^{z+} is complexed [125,134–138] with such a crown in the presence of an anion which is either self-stabilized or is stabilized through bonding with a strong proton donor such as water. The 1 : 2 M^{z+}–crown encapsulates which have been revealed through X-ray analysis to be genuine sandwich encapsulates are $[Na(12C4)_2](Cl,5H_2O)$ [134], $[Na(12C4)_2](OH,8H_2O)$ [135], $[Na(12C4)_2]ClO_4$ [136], $[Na(12C4)_2]NCS$ [137], $[Na(B15C5)_2]ClO_4$ [138], $[Na(B15C5)_2]BPh_4$ [138], $[K(B15C5)_2]I$ [129], $[K(B15C5)_2]$pic [130], $[K(B15C5)_2](dnb \cdot 2Hdnb)$ [131], $[Cs(15C5)_2]I$ [132], $[Cs(18C6)_2]^+$ moiety of the complex $[Cs_9(18C6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}$ $[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$ [139], [Cs(DBTM18C6*trans–anti–trans–trans*)$_2$]NCS [140] and $[Ba(15C5)_2](Br_2,2H_2O)$ [125]. All such K^+ sandwiches are shown in Fig. 4. The sandwich $[K(B15C5)_2](dnb \cdot 2Hdnb)$ [131] has the distinction of being the first crystallographically characterized M^{z+}–crown complex involving a homoconjugated organic anion. It should, however, be stressed that the presence of two molecules of a crown for a cation does not necessarily convey sandwich encapsulation. Structural analysis (Fig. 5) of the complex $Ca(dnb)_2(B15C5)_2 \cdot 3H_2O$ [114] (Section B (ii) (c) type (i)), for instance, reveals merely a 1 : 1 complexation.

Earlier [40,141], formation of the sandwich encapsulates was attributed only to a larger size of the cation as compared with that of the crown cavity (ion–cavity radius concept or ion–cavity size relationship). We, however, argued [9,11] the formation of such complexes to be a consequence of the incorporation of the superchelate effect of the rather highly basic donor ring on the polarizable cation (ligand encapsulation); in the case of a counter-anion like NCS^-, such a charge separation of the complexed cation could also be because of the steric blockade by the crown molecules to the anion [9]. Formation of $[Cs(15C5)_2]I$ [132], for example, may be related entirely to the operative ligand encapsulation while for a complex such as [Cs(DBTM18C6

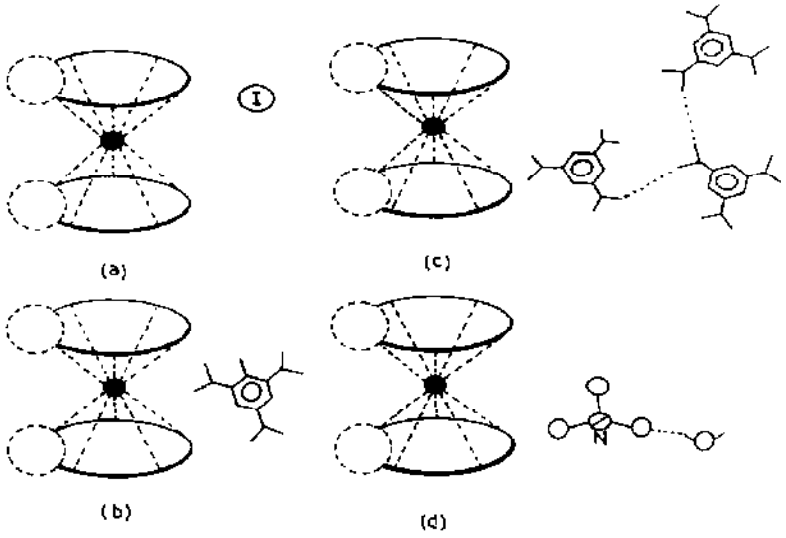


Fig. 4. A schematic view of K^+ sandwich encapsulates: (a) $[K(B15C5)_2]I$; (b) $[K(B15C5)_2]pic$; (c) $[K(B15C5)_2](dnb \cdot 2Hdnb)$; (d) $[K(B15C5)_2]NO_3 \cdot H_2O$.

trans–anti–trans–trans)$_2$]NCS [140] the blockade factor may also contribute.

As and when a low charge density M^+ (K^+, Rb^+ and Cs^+) forms a sandwich encapsulate, the significant point is that the complex crystallizes in the 1 : 2 stoichiometry even when the salt–crown reaction mixture is 1 : 1 [91] and the complex in solution is also 1 : 1 [142]. The 1 : 1 reaction mixture works for a 2 : 2 system from which one equivalent of the salt separates uncomplexed. Efforts to force a 1 : 1 complexation of K^+ with the 15C5 ring through substitution of aliphatic and aromatic moieties on the ring have also failed and K^+ has yielded a sandwich, irrespective of the nature of the substituents and the synthesis medium used [102]. Furthermore, under favourable conditions ("non-interacting" anion), the ligand-encapsulated Cs^+ is noted to generate sandwiches with the rather size-compatible 18C6

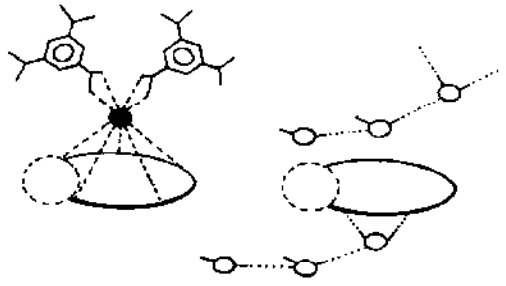
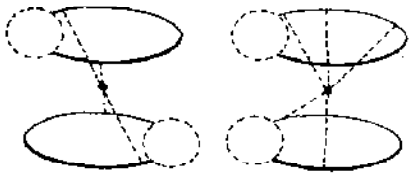


Fig. 5. A schematic view of $[Ca(dnb)_2(B15C5)](B15C5,3H_2O)$.



(a) (b)

Fig. 6. A schematic view of (a) $[Na(B15C5)_2]ClO_4$ and (b) $[Na(B15C5)_2]BPh_4$.

[139] as well as with the smaller cavity 15C5 [132] even though the self-encapsulating ability (i.e. polarizing ability [11]) of this cation is poor. In view of these points, it appears that the charge separation of such a cation is because of its own inherited interactive characteristics related to its Lewis acid status and is not a consequence of just its size relative to the cavity size, as is held (for example, ref. 138) even today.

Essentially because of the effective cation–oxygen contacts, a small crown such as 12C4 tends to yield 1 : 2 charge-separated complexes with the higher charge density Na^+ in the presence of various anions such as ClO_4^- [136], NCS^- [89,96,137], and even Cl^- [134] or OH^- [135]; for Cl^- and OH^-, stabilization through bonding with the reaction medium should be a pronounced cooperative effect. Solvation of the cation and the crown can be restricted through the use of a concentrated reaction medium. Cooperation of self-encapsulation by the cation and the macrocyclic effect of the crown does help charge separation of Na^+ from the charge-delocalized anions such as ClO_4^- and BPh_4^-. In the sandwich encapsulates so obtained [94,143], however, all the crown oxygens may not be involved in binding the cation as seen through X-ray analysis [138] of $[Na(B15C5)_2]ClO_4$ and $[Na(B15C5)_2]BPh_4$ (Fig. 6). The reason for sandwich formation for a still higher charge density Ba^{2+} in the system $[Ba(15C5)_2](Br_2,2H_2O)$ [125] can be understood in view of self-encapsulation by Ba^{2+}, enhanced basicity of the unsubstituted 15C5, and stabilization of Br^- through bonding with water molecules. Regarding the 1 : 2 complexes of the still higher charge density Ca^{2+}, viz. $Ca(pic)_2(B15C5)_2$ and $Ca(BPh_4)_2(B15C5)_2$ [108], charge separation may not have taken place as noted [114] for $Ca(dnb)_2(B15C5)_2 \cdot 3H_2O$ (Fig. 5).

For a large cation and a small cavity crown (B15C5 in particular), the formation of 1 : 2 complexes has frequently been noted. For B15C5 such complexes are $KNCS(B15C5)_2 \cdot MeOH$ [108], $KClO_4(B15C5)_2$ [143], $CsClO_4(B15C5)_2$ [143], $CsBPh_4(B15C5)_2$ [94], $Sr(ClO_4)_2(B15C5)_2$ [108] and $Ba(NCS)_2(B15C5)_2$ [85] which stand the chance of being charge separated. Anions such as BPh_4^- and ClO_4^- form rather "inert" (insoluble) ion pairs with the low charge density K^+ and Cs^+, yet their sandwich encapsulation

takes place. Sr^{2+} and Ba^{2+}, which exploit the macrocyclic effect because of a stronger self-encapsulating ability, manage their sandwich encapsulation as and when the anion permits. Thus for pic^-, Sr^{2+} and Ba^{2+} form isomorphous 1 : 1 ion-paired complexes [120,121] which is apparently the dictation of the anion. Polarizability as well as the self-encapsulating ability of K^+ is adequate to favour its sandwich encapsulation in the presence of pic^- [146] but in opposition to the ion–cavity radius concept, Rb(pic) and Cs(pic) yield anion-paired complexes of the type M(pic)(B15C5) [144,145] (details Section B (ii) (c) type (iii)).

The 2 : 3 complexes, so-called club sandwiches [85], illustrated in Fig. 3(b), are more rarely encountered yet they constitute a definite category of the M^{z+}–crown encapsulates. Such complexes are usually undefined but crystalline species such as $(Na(pic))_2(DB14C4)_3$ [95], $(Na(tos))_2(18C6)_3$ [88], $(CsNCS)_2(B18C6)_3$ [85], $(CsNCS)_2(DB18C6)_3$ [85] and $(Cs(tcnq))_2(18C6)_3$ [99,100] are fairly stoichiometric. The 2 : 3 interaction, intriguingly, does not appear to offer any advantage for the purpose of electrostatic stabilization of M^{z+} or of the crown over the one possible with the help of 1 : 2 sandwich formation [11]. Another difficulty in simulating this stoichiometry is that the crown molecule located in the middle of the system cannot be visualized to maintain equally effective M^{z+}–O contacts on both axial sides at one time. X-ray analysis [146] of the complex $(Rb_{0.55}Na_{0.45}NCS)_2(DB18C6)_3$, which was originally reported by Pedersen as $RbNCS(DB18C6)_2$ [85], has indeed revealed the system to be [RbNCS(DB18C6)] plus [Na(DB18C6)]NCS plus an uncomplexed DB18C6. Other systems reported to have a 2 : 3 stoichiometric interaction are $(CsI_3)_2(DC18C6)_3$ [85] and $[Mg(tcnq)_2TCNQ]_2(15C5)_3 \cdot 2H_2O$ [123] in each of which the additional crown molecule is held loosely in the lattice.

Earlier we have argued [11] that there cannot be an obvious chemical interactive requirement to form a club sandwich. However, the desire to show something new has prompted some workers to illustrate formation of club sandwiches. Recently, Vidal et al. [139] have presented $[Cs_2(18C6)_3]^{2+}$ along with $[Cs(18C6)_2]^+$ and $[Cs(18C6)CO]^+$ (Fig. 7) in the high nuclearity rhodium-cluster $[Cs_9(18C6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$. These researchers have been tempted to class the entity as a "novel first characterized genuine triple decker or a club sandwich". In fact, the observations which can be made on the overall molecule are the following. (i) Within the cluster there is a variety of lattice packing schemes for the Cs^+–18C6 entities. (ii) For the Cs^+–crown combination in the "club sandwich", the Cs^+–O(crown) distances are very different from those in 1 : 1 and 1 : 2 moieties within the same system; even the two types of $[Cs(18C6)_2]^+$ sandwiches existing in the cluster concerned differ from each other in this regard. (iii) The "club-sandwich" moiety displays much longer (average 3.79

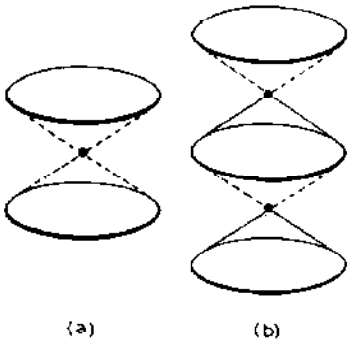


Fig. 7. A schematic view of (a) $[Cs(18C6)_2]^+$ and (b) $[Cs_2(18C6)_3]^{2+}$ moieties present in the cluster $[Cs_9(18C6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$.

and 4.03 Å) Cs^+–O(crown) contacts (shown broken) than the normal bonding distances (3.03–3.34 Å [9]) for the Cs^+–crown systems. Apparently, the moiety–moiety interactions in the lattice leads to formation of new systems under the forced conditions to yield additive products such as the "triple decker" in the present system. Such a formulation in the lattice is made possible by the symmetry and flexibility of the crown molecule which can sense electrophilic effects from both the axial sides (even simultaneously) as would be envisaged towards the formation of a "club sandwich".

The 1 : 1 wrap-around encapsulation, illustrated in Fig. 3(c), is another mode of charge separation. The wrap-around encapsulates are usually formed by a large-cavity crown such as DB30C10 with a low charge density cation such as K^+ [147,148] or Rb^+ [149]. The complex [K(DB30C10)]I (Fig. 8) is a historical example [147]. Charge separation of such a cation is the result of ligand encapsulation (aided by its self-encapsulation) with the macrocycle and its tendency to strip off the anionic species. In the complexes [K(DB30C10)]NCS [148] and [Rb(DB30C10)]NCS · H_2O [149] (Fig. 8), the anion is solvated only in the latter complex. Wrap-around encapsulation [150] of the rather anionphilic Na^+ in the complex [Na(*asym*-DB24C8)]ClO_4 (Fig. 9) appears favoured by the asymmetry of the ligand and charge-delo-

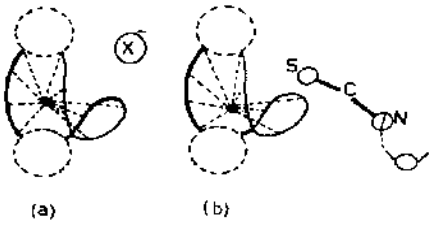


Fig. 8. A schematic view of wrap-around encapsulates: (a) [K(DB30C10)]I or [K(DB30C10)]NCS (X^- stands for I^- or NCS^-) and (b) [Rb(DB30C10)]NCS·H_2O.

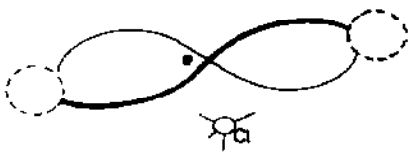


Fig. 9. A schematic view of [Na(*asym*-DB24C8)]ClO_4.

calization of the counter-anion. Under most conditions, however, a higher charge density cation should generate an incomplete wrap-around encapsulate (type (ii) in Section B (ii) (c)) as noted for $Ba(ClO_4)_2$(DB24C8) [112] and $Ba(pic)_2$(DB24C8) · $2H_2O$ [118] and speculated for the complexes NaX(DB24C8) · H_2O (X = Cl, Br or NCS) [90]. The cavity size of the rather flexible 18C6 should in principle be enough for wrap-around encapsulation of a small cation such as Li^+. However, X-ray results on the "complex" $[Li(18C6)(H_2O)_2]ClO_4$ [151] suggest that the compound is merely $LiClO_4$ partially dehydrated by the crown; $LiClO_4 \cdot 3H_2O$ [152] is itself a charge-separated "solvent complex" [9] and the present system is a less hydrated $LiClO_4$ which carries the crown molecule through incomplete coordination by the cation.

(b) Cation–cavity compatible anion-separated encapsulates

Such encapsulates are by implication planar or roughly planar and are 1 : 1. Herein the anion exhibits no direct contact with the counter-cation (Fig. 3(d)) while the cation may or may not be coordinated by one or more solvent molecules as illustrated in Fig. 10. The encapsulate [Na(B15C5)-(H_2O)]I [128] represents a case wherein the axial position is filled with a water molecule (Fig. 10) displaying "double action" [9] and holding an iodide with its polar proton. Since the anhydrous analogue of the complex cannot be synthesized, incorporation of the water molecule in the complex is a chemical requirement for the displacement of I^-. The encapsulates [K-(18C6)]NCS [153] and [K(N20C6)]NCS [154] are of the type where NCS^- is disordered and does not exhibit its usual N-bonding mode (Fig. 10) but the cation does not derive any solvent molecule. This disordering of NCS^-,

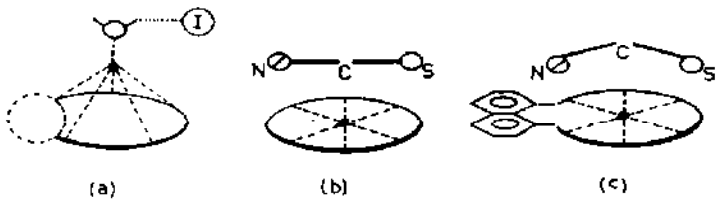


Fig. 10. A schematic view of selected cation–cavity compative anion-separated encapsulates: (a) [Na(B15C5)(H_2O)]I; (b) [K(18C6)]NCS; (c) [K(N20C6)]NCS.

despite K^+–N(S) distances being quite short (Table 1) may be treated as equivalent to "anion separation". Out of the two moieties [K(DB18C6)(H_2O)]I and [KI(DB18C6)] of the complex KI(DB18C6) · $\frac{1}{2}H_2O$ [155] anion separation in the former appears aided by co-interaction of the water molecule from an axial direction. However, in the complex of the rather anionphilic Na^+ with the same rather less basic crown, viz. NaBr(DB18C6) · $2H_2O$ [156], anion separation in the moiety [Na(DB18C6)(H_2O)$_2$]Br is basically a consequence of the Br^- being involved with the polar protons of the Na^+-coordinated water molecules. This should obviously also be the reason for anion separation in the systems [Na(18C6)(H_2O)]NCS [157] as well as [Na(DC18C6 *cis–anti–cis*)(H_2O)$_2$]Br [158] and in the moieties [Na(18C6)(THF)$_2$]$^+$ of the complexes Na(P(CN)$_2$)(18C6) · THF [159] and [Na(18C6)(THF)$_2$]$_2$[P_2(CN)$_6X_2$] (X = Br or I) [160]. For the other higher charge density cations such as Ca^{2+} and Sr^{2+} anion separation can also be related to solvation of the cation with the water molecules as revealed for the complexes [Ca(12C4)(H_2O)$_4$](Cl_2,$4H_2O$) [124] and [Sr(B18C6)(H_2O)$_3$](ClO_4)$_2$ [111]. However, for all such higher charge density cations, a coordinated water molecule should work for an "anion" and each system may be treated as a pseudo-anion-paired encapsulate.

The moiety [Na(DB18C6)]NCS in the complex ($Rb_{0.55}Na_{0.45}NCS$)$_2$(DB18C6)$_3$ [146] constitutes a rather intriguing case wherein the higher charge density Na^+ becomes anion separated even without the involvement of any solvent molecule and particularly when the cation is not tightly complexed in the rather large and poorly basic donor ring. To determine if this could be the structural effect of the co-presence of the Rb^+-complex moiety in the system, we are interested in the re-structural analysis of the pure NaNCS–DB18C6 complex.

(c) Anion-paired encapsulates

An encapsulate of this category can be of the following type: (i) a 1 : 1 complex of a cation with a crown of the cavity size comparable to that of the cation as illustrated in Fig. 3(e); (ii) a 1 : 1 complex of a cation of the partial wrap-around type (incomplete encapsulate) with a crown of the cavity size distinctly exceeding that of the cation as illustrated in Fig. 3(f); (iii) a 1 : 1 complex of a cation with a crown of the cavity size much less than that of the cation; (iv) a bimetallic 2 : 1 complex of two smaller cations with a rather large cavity crown as illustrated in Fig. 3(g); (v) a 2 : 2 dimeric anion-paired encapsulate as illustrated in Fig. 3(h) (see also Table 1).

Among the anion-paired encapsulates, those of type (i) are the most frequently encountered. The cation whose size is comparable to that of the crown cavity fits into the latter while permitting interaction with the

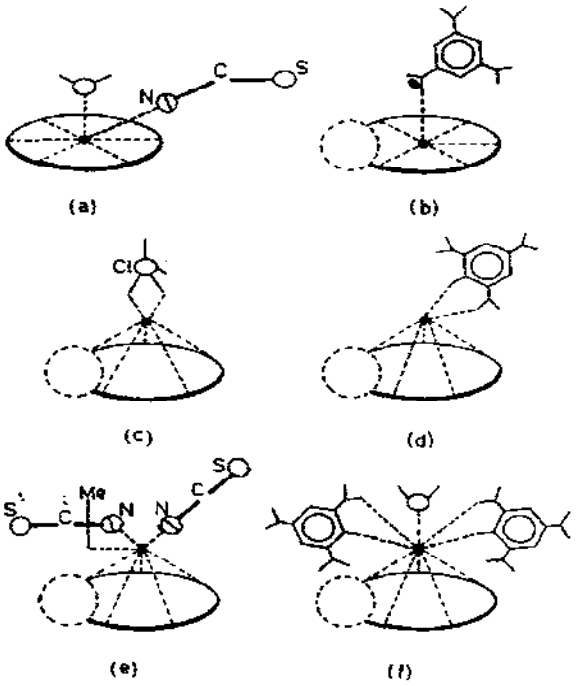


Fig. 11. A schematic view of selected cation–cavity comparable anion-paired encapsulates: (a) [NaNCS(15C5)(H_2O)] moiety of NaNCS(15C5)·$\frac{1}{2}H_2O$; (b) Na(dnb)(B15C5)·H_2O; (c) $NaClO_4$(B15C5); (d) Na(pic)(B15C5); (e) $Ca(NCS)_2$(B15C5)·MeOH; (f) $Ba(pic)_2$(B15C5)·H_2O.

counter-anion(s) from the axial sides. Such M^{z+}–crown encapsulates (Fig. 11), wherein the cation–anion pairing has been confirmed through X-ray structural analysis are LiNCS(12C4) [161], LiNCS(B13C4) [162], $LiClO_4$(B13C4) [163], Li(pic)(B13C4) [163], LiNCS(DB14C4) [164], LiNCS(16C4) [165], NaNCS(15C5) · $\frac{1}{2}H_2O$ (possessing two types of anion-paired moieties, viz. [NaNCS(15C5)] and [NaNCS(15C5)(H_2O)]) [166], Na(eaa)(15C5) [167] (where eaa^- = ethylacetoacetato anion), $NaClO_4$(B15C5) [138], Na(pic)(B15C5) [168], Na(dnb)(B15C5) · H_2O [169], NaNCS(DB18C5) [170], $Na(P(CN)_2)$(18C6) · THF (in its moiety $[Na(P(CN)_2)_2$(18C6)$]^-$) [159], $Na(W(CO)_5(SH))$(18C6) [171], $Na(W_2(CO)_{10}(\mu\text{-}SH))$(18C6) [171], NaBr(DB18C6) · $2H_2O$ (in its moiety [NaBr(DB18C6)(H_2O)]) [156], K(tos)(18C6) [126], K(eaa)(18C6) [172], KI(DB18C6) · $1/2H_2O$ (in its moiety [KI(DB18C6)]) [155], KI(DB18C6) · thiourea [173], $K(Al_2Me_6Cl)$(DB18C6) · $2C_6H_6$ [174], $Mg(NCS)_2$(B15C5) [110], $Ca(NCS)_2$(B15C5) · H_2O [110], $Ca(NCS)_2$(B15C5) · MeOH [110], $[Ca(dnb)_2$(B15C5)](B15C5,$3H_2O$) [114], $Ca(NCS)_2$(18C6) [107], $Sr(pic)_2$(B15C5) · H_2O [120], $Ba(pic)_2$(B15C5) · H_2O [121], $Ba(ClO_4)_2$(B18C6) · $2H_2O$ [111] and $Ba(NCS)_2$(DC18C6 *cis–syn–cis*) · H_2O [106]. Evidently, pairing of the cation with the counter-anion is a

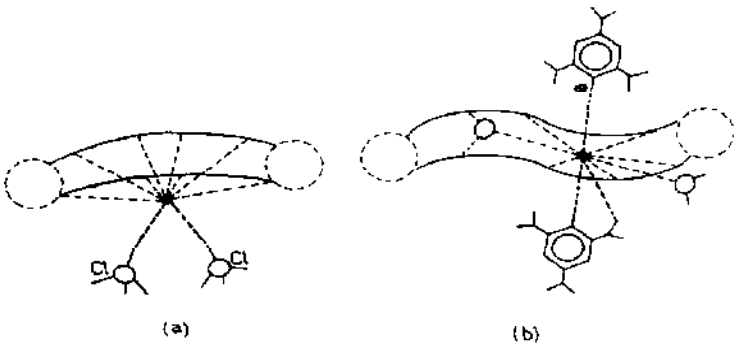


Fig. 12. A schematic view of incomplete wrap-around encapsulates: (a) $Ba(ClO_4)_2(DB24C8)$ and (b) $Ba(pic)_2(DB24C8)\cdot 2H_2O$.

feature of the encapsulates of especially the higher charge density M^{z+} such as Li^+, Na^+ and Ca^{2+}. This feature is aided when the counter-anion is strongly associating such as NCS^- or is chelating such as a nitrophenolate. The lower charge density cations, on the other hand, tend to undergo anion separation as has been discussed in Section B (ii) (b). However, if the counter-anion is chelating and/or the basicity of the crown donor ring is reduced through appropriate substituents, ion pairing can also be imposed on a low charge density cation, as noted for the complexes K(tos)(18C6) [126], K(eaa)(18C6) [172], KI(DB18C6) · thiourea [173] and $K(Al_2Me_6Cl)(DB18C6)\cdot 2C_6H_6$ [174], or for the [KI(DB18C6)] moiety of $KI(DB18C6)\cdot 1/2H_2O$ [155].

An incomplete encapsulate (type ii) that exhibits partial wrap-around of the rather "anionphilic" (high charge density) cation is formed by a crown of the not-so-large cavity such as DB24C8. The complexes $Ba(ClO_4)_2$ (DB24C8) [112], $Ba(pic)_2(DB24C8)\cdot 2H_2O$ [118] and perhaps NaNCS $(DB24C8)\cdot H_2O$ [90] exemplify the system (Fig. 12). Such behaviour of the encapsulate is perhaps because the crown ring is not large enough to cause complete wrap-around of the cation, especially under the competitive effect of the anionic species.

The anion-paired encapsulates of type (iii) (Fig. 13), for which the crown cavity is distinctly smaller than the cation, are rather new. So far only two complexes, Rb(pic)(B15C5) [145] and Cs(pic)(B15C5) [144], have been recognized to exhibit ion-paired interaction conforming to the above conditions. The formation of these encapsulates has undervalued the ion–cavity radius concept with regard to the solid state stoichiometry of these complexes and has opened new vistas in our understanding of the interactive characteristics of the M^{z+} ions.

The coordination number of Cs^+ is in general 8 to 10 [9]. In the system Cs(pic)(B15C5) the cation does exhibit 9-fold coordination but does not

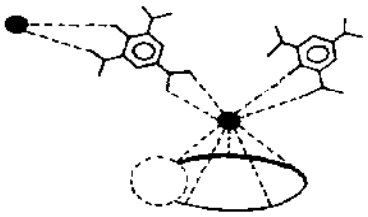


Fig. 13. A schematic view of a large-cation anion-paired encapsulate, viz. Cs(pic)(B15C5).

choose to generate a sandwich encapsulate. This could have been expected in view of the ion–cavity radius concept. While in a state paired by its counter-anion (Cs^+–O^-, 3.03 Å and Cs^+–O(*o*-NO_2), 3.01 Å) the cation exhibits unusual chelation by the *p*-nitro group of the pic^- of the adjoining molecule in the lattice (Cs^+–O, 3.16 and 3.42 Å); the Cs^+–O(crown) distances are in the range 3.00–3.24 Å. This anion effect of the charge neutralizer (pic^-) has even forced Rb^+ to form an isomorphous system although under most conditions it exhibits (mimics) the chemistry of K^+ [175].

The anion-paired species can also be obtained for the large-cavity crowns but in the form of 2 : 1 bimetallic species (type iv, Fig. 14), wherein the two cations prevent the folding of the crown ring and accept the anions from the axial sides. The formation of a bimetallic 2:1 encapsulate is also not as much a function of the cation–cavity size relationship as it is of the anion–cation pairing strength of the complexed cation. Thus, with the large-cavity DB30C10, the anionphilic Na^+ forms bimetallic complexes $(NaNCS)_2$(DB30C10) [176] and $(NaI)_2$(DB30C10) [90] which is unlike the low charge density K^+ which prefers charge separation in the analogous reaction systems (Section B (ii) (a)). When charge separation of the cation is unfavourable, say in the total absence of water from the reaction conditions, then formation of the anion-paired bimetallic compounds also becomes feasible for a low charge density cation (K^+) as noted through structural

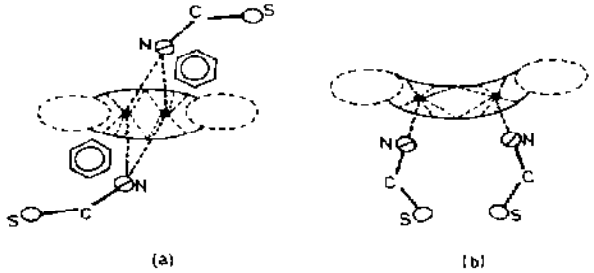


Fig. 14. A schematic view of selected bimetallic 2 : 1 complexes: (a) $(KNCS)_2$(DB24C8) and (b) $(NaNCS)_2$(DB30C10).

analysis of the systems $(KNCS)_2(DB24C8)$ [177,178] and $(Na(onp))_2$ (DB24C8) [179] (where $onp^- = 2$-nitrophenolate). The anion contribution of pic^- anions is dominating in the system $Ba(pic)_2(DB24C8) \cdot 2H_2O$ [118] which cannot become bimetallic not only because pic^- is chelating but also because it is bulky.

The complex $(LiNCS)_2(18C6) \cdot 2H_2O$ [151], which is unfortunately poorly described (and illustrated) by the author, is in fact not a genuine bimetallic complex. It is that peculiar Li^+–system wherein the nucleophilic species of the original salt, i.e. NCS^- and water molecules have undergone major disproportionation because of the participation of some of the crown oxygens. The thiocyanate anion of one lithium ion, Li(1), which interacts with two crown oxygen atoms, has been pushed to the other lithium ion, Li(2), which in turn interacts with only one crown oxygen and forms part of an anionic moiety. The 4-coordination sphere of Li(1) consists of two crown oxygen atoms and two water oxygen atoms while that of Li(2) is from one crown oxygen, one water oxygen and two nitrogens of two different NCS^- anions. The system $(Co(salen)Na)_2(DC18C6$ *cis–anti–cis*) (Fig. 15) [180] (where salen = *N,N′*-ethylenebis(salicylideneaminato)) is also not a bimetallic complex in the true sense of the description, although the crown molecule is in direct touch with two Na^+ ions (one from each axial direction). The crown molecule appears to have inserted itself between the two molecules of [Co(salen)Na(CO_2 or THF)] and because of its multichelating nature, strips off Na^+ from CO_2 or THF. The crown acts as a bridge between these moieties so that three of its oxygens are symmetrically coordinated to each Na^+ ion.

The dimeric anion-paired encapsulates (type v and Fig. 16) are unique in that although they are analysed for 1 : 1 stoichiometry [92], X-ray structural analysis reveals them to be 2 : 2 [140,181–183]. Until recently, we recognized [9] this category only for the complexes of the larger Rb^+ and Cs^+ with

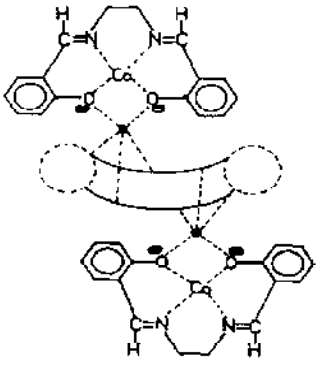
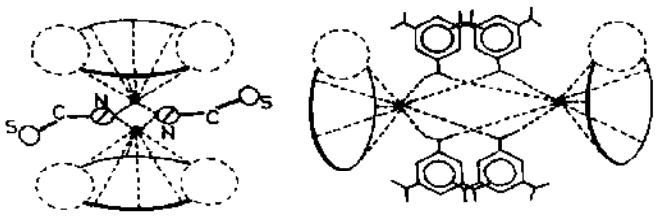


Fig. 15. A schematic view of "bimetallic" $(Co(salen)Na)_2(DC18C6$ *cis – anti – cis*).



(a) (b)

Fig. 16. A schematic view of selected dimeric, viz. 2:2 complexes: (a) [CsNCS(DBTM18C6 *cis–anti–cis–anti*)]$_2$ and (b) [Ba(dnb)$_2$(B15C5)]$_2$.

crowns of the 18C6-cavity size. Dimerization of the 1:1 moieties takes place through a suitable anionic site in particular through that of the bridging NCS^-, as displayed by the complexes [RbNCS(18C6)]$_2$ [181], [RbNCS(B18C6)]$_2$ [182], [CsNCS(18C6)]$_2$ [183] and [CsNCS(DBTM18C6 *cis–anti–cis–anti*)]$_2$ [140]. Interestingly, in the complexes of the ligand NO_2-B18C6 (**XIX**) (Section C (iii), a category 3 crown-related macrocycle), viz. [RbNCS(**XIX**)]$_2$ and [CsNCS(**XIX**)]$_2$, the nitro-oxygens are involved in dimerization with or without the co-participation of NCS^-. Formation of a 2:2 anion-paired encapsulate is apparently an alternative to that of the expected charge-separated sandwich. For those complexes wherein NCS^- is the bridging anion, dimerization has been attributed [9] to (i) the associating tendency of NCS^- with the cation and (ii) the optimum anionphilicity of the M^+–crown moiety which is suited for pairing of NCS^- with it. In each such system, NCS^- bridges the two cations through the N-end and one of the two M^+–N contacts (Table 1) is consistently shorter than the other.

Recently we have characterized a novel 2:2 system involving a smaller crown and an organic anion [115], i.e. [Ba(dnb)$_2$(B15C5)]$_2$ (Fig. 16). In view of its non-crystalline nature, it has not been possible to establish whether the analogous Sr^{2+} system is isostructural with it. However, the Ca^{2+} complex, viz. [Ca(dnb)$_2$(B15C5)](B15C5,3H$_2$O) [130], exists in discrete 1:1 entities (Fig. 5). The system [Ba(dnb)$_2$(B15C5)]$_2$ is rather intriguing in that the dnb^- anions bridge (Ba^{2+}–O^-, 2.64–2.69 Å) between the two Ba^{2+} ions instead of chelating the respective ions as noted for the Ca(dnb)$_2$ system [114]. The size of the cation is not the only factor, however. The complex of K(dnb), viz. [K(B15C5)$_2$](dnb · 2Hdnb) [131] is, for example, a genuine charge-separated sandwich encapsulate, although the charge-separated dnb^- exhibits a high nucleophilicity and has to generate dnbH through deprotonation of the protic medium for the purpose of forming a stable homoconjugate, dnb,2dnbH (Fig. 4(c)).

The mere existence of two cations and two crown molecules in a molecule of a complex does not necessarily mean dimerization. Thus, the complexes

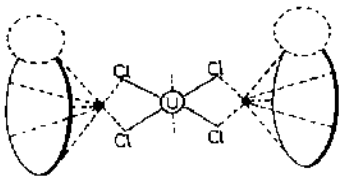


Fig. 17. A schematic view of Na_2(tetrachlorodioxouranate)(B15C5)$_2$ which is not a dimeric complex.

Na_2(tetrachlorodioxouranate)(B15C5)$_2$ [184] (Fig. 17), K_2(phthalocyanine)(18C6)$_2 \cdot 1.5C_6H_6$ [185] and $K_2(Mo_6O_{19})(18C6)_2 \cdot H_2O$ [186] are not dimeric species although each of them may be regarded as a 2 : 2 ion-paired complex. The complexes $K_2(Pt(CN)_3R)(18C6)_2$ (R = a variety of σ-carbyl ligands), $K_2(PtH(CN)_3)(18C6)_2$ and $K_2(Pt(CN)_3(SiPh_3))(18C6)_2$ [103] are also expected to fall in this category. The counter-anion in these systems being dinegative carries two cations each of which has no alternative except to complex with a molecule of crown. In such systems, the chemistry of the anion becomes the key factor. Some unusual forces may be imposed on the complexed cation as through the bridging of two Cl^- moieties with one Na^+ [184] or through coordination of water and hexamolybdate oxygens with the crown-stabilized K^+ [186]. In the complex $K_2MoO_4(18C6)_2 \cdot 5H_2O$ [187], however, the molybdate anion carries only one cation as revealed by the existence of two distinct charged moieties $[K(18C6) \cdot 2H_2O]^+$ and $[KMoO_4(18C6) \cdot H_2O]^-$ in the complex. The failure of MoO_4^{2-} to carry two cations may be attributed to a lower chelating order than that of $Mo_6O_{19}^{2-}$ so that only one K^+ is forced to form an anion-paired complex while the other cation is free to produce an anion-separated moiety. In an analogous Na^+ system, however, the anionphilic cation could possibly fail to produce the anion-separated moiety. In the complex $Na(P(CN)_2)(18C6) \cdot THF$ [159], which exists in the form of two different charged moieties $[Na(P(CN)_2)_2(18C6)]^-$ and $[Na(18C6)(THF)_2]^+$, formation of the latter moiety appears to be a consequence of the former which develops a negative charge because of two $P(CN)_2^-$ anions.

(d) Products carrying non-chelated crowns

Crystalline products carrying non-chelated crowns have also been characterized crystallographically. For a salt derived from a higher charge density cation and a chelating or a highly nucleophilic anion, a crown can be crystallized along with the salt without cation–crown chelation having taken place. A situation of this type has been revealed for $(Rb_{0.55}Na_{0.45}NCS)_2$(DB18C6)$_3$ [146] wherein, of course, cation-chelated crowns also exist. The complex [Ca(dnb)$_2$(B15C5)](B15C5,3H_2O) [114] represents a system (Fig. 5) wherein one of the two crown molecules is not chelated with the cation. A

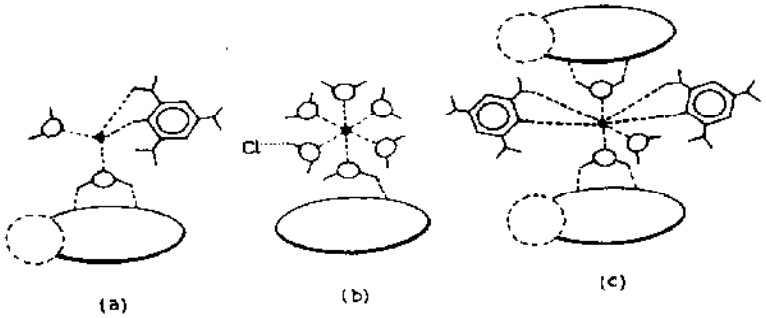


Fig. 18. A schematic view of products wherein the M^{z+}–crown interaction is missing: (a) $[Li(pic)(H_2O)_2]B15C5$; (b) $[Mg(H_2O)_6](12C4)Cl_2$; (c) $[Ca(pic)_2(H_2O)_3]B15C5$.

total lack of cation–crown chelation (Fig. 18) has been noted for the products $[Li(pic)(H_2O)_2]B15C5$ [188], $[Mg(H_2O)_6](12C4)Cl_2$ [189] and $[Ca(pic)_2(H_2O)_3]B15C5$ [190]. In such systems, the highly basic nature of the crown ring, i.e. its ability to interact with the feebly cationized water protons appears to disfavour chelation of the crown ring with water-coordinated [189] or water- and anion-coordinated [188,190] cations.

In conclusion, discrimination of M^{z+} in the solid M^{z+}–crown systems can be ascribed to the differences they display with regard to the crown/anion preferences determined essentially through X-ray structural analysis. For the M^{z+}–crown systems with or without solvent molecule(s), the cation can show any of the following types of interactions with respect to the crown: (i) exclusive interaction with the crown—complete encapsulation ("charge separation"); (ii) interaction with the crown as well as the anionic species including the solvent molecule(s)—ion-paired 1 : 1, 2 : 2 or 2 : 1 encapsulation ("ligation"); and (iii) exclusive interaction with the anionic species—"non-chelation".

(iii) General principles determining M^{z+}–crown interaction in solid state

The interaction principles involved in the M^{z+}–crown systems can be understood more through understanding the interaction stoichiometry. Until recently, however, this important parameter had been considered [40,141] to be essentially a function of the cation size in relation to the cavity size of the macrocycle. Thus, (i) formation of the 1 : 1 non-wrap-around complexes had been attributed to the right fit of the cation in the cavity of the crown, (ii) formation of the bimetallic 2 : 1 as well as 1 : 1 wrap-around complexes had been attributed to the cavity size of the crown being for greater than the cation size, (iii) formation of the 1 : 2 sandwich complexes had been attributed to the cation size being greater than the cavity size. One of us has argued [11] at length that this concept is not correct. In fact, the stoichiome-

try of a given M^{z+}–crown system can be controlled through a variation in the nature of the counter-anion and the solvating medium from which the synthesis is carried out [11]. Also, (i) two cations of comparable size (K^+ and Ba^{2+}) can form the complexes of differing stoichiometry with a crown for a given counter-anion, pic^- [121,130]; (ii) a cation (Na^+) of size not necessarily exceeding the cavity size of the complexing crown (B15C5) can also yield a 1 : 2 sandwich [138]; (iii) a not-so-large cavity crown (DB24C8) can yield a bimetallic 2 : 1 species [177,178] while with the same salt (KNCS) a larger cavity crown (DB30C10) can consistently produce a 1 : 1 species.

Examination of the available X-ray results for the M^{z+}–crown complexes reveals that chelation of cation(s) with the crown usually involves all the donor oxygens of the crown molecule(s) but the crown/anion preferences of the cation in the lattice depend on (a) the charge density of the cation which increases in the order Cs^+ to Li^+ and Ba^{2+} to Mg^{2+}, (b) the charge localization/delocalization and interacting mode of the counteranion, (c) the nature of the donor ring with respect to the number of interacting oxygens it carries and the molecular flexibility it displays, and (d) the presence of a neutral co-ligand such as a solvent molecule in the lattice. The following treatment delineates the importance of these factors.

(a) The cation contribution

The cation contribution is easily detectable. The cation determines its own complexation in two ways: (i) it exercises an effect related to its "hardness" on the counter-anion and is associated with the latter accordingly—an involvement which is unfavourable to its complexation as is obvious from the aforementioned results for M^{2+} vis-a-vis those of M^+; (ii) it exercises its Lewis acidity (charge density) effect in modifying the conformation of the complexing macrocycle and in calling into play ion–dipole forces with the donor oxygens. Weak Lewis acids (K^+, Rb^+ and Cs^+) interact weakly with the anion and allow the crown to bind them (ligand encapsulation). For the stronger Lewis acids the anion effect has to be reduced to make their charge density operate on the crown (self-encapsulation). These points are supported by the following observations.

Potassium picrate yields a 1 : 2 sandwich with B15C5 [130] in quite the same way as KI [129] does (even for the 1 : 1 reaction mixtures) whereas $Ba(pic)_2$ only forms a monohydrated 1 : 1 ion-paired complex with the same crown even for the 1 : 2 reaction mixtures [121], although Ba^{2+} is approximately the size of K^+. This is true even though Ba^{2+} is a divalent cation and could have reflected self-encapsulation in forming a sandwich as in $[Ba(15C5)_2](Br_2,2H_2O)$ [125] and possibly also in $Ba(NCS)_2(B15C5)_2$ [85] and $Ba(ClO_4)_2(B15C5)_2$ [108].

The B18C6 complex with $Ba(ClO_4)_2$ is anion paired [111] while that of $Sr(ClO_4)_2$ is anion separated despite little difference in the Lewis acid status of these two congeners. Also, in the complex $Mg(NCS)_2$(B15C5) [110] the two anions fill both the axial positions of the donor ring while in $Ca(NCS)_2$(B15C5) · H_2O [110] both the anions approach the cation from the same axial side. This suggests that $Mg(NCS)_2$ undergoes a transitory ionization during complexation while $Ca(NCS)_2$ undergoes complexation as a bent angular "un-ionized" species.

With each of B15C5 and DB30C10, a lower charge density cation such as K^+ undergoes charge separation while the higher charge density Na^+ maintains contact with the solvent [128] or the counter-anion [176]. Furthermore, with DB18C6 as the complexing crown, Rb^+ maintains contact with NCS^- but, unexpectedly, Na^+ becomes charge separated [146]. The ion pairing displayed by Rb^+ in the moiety RbNCS(DB18C6) in the complex $(Rb_{0.55}Na_{0.45}NCS)_2(DB18C6)_3$ can in no way, however, be regarded as its truly original behaviour because of other effective interactions. In the complex KI(DB18C6) · $\frac{1}{2}H_2O$ [155], involving the same crown and the best-fit K^+, the moiety [K(DB18C6)(H_2O)]I is anion separated while the anhydrous moiety [KI(DB18C6)] is anion paired. The rather loose fit Na^+ in the Rb^+–Na^+ complex is separated from the cationphilic NCS^- but not the better fit K^+ from the weakly cationphilic I^- in the same complex unless the water molecule is also coordinated to the cation. Obviously, therefore, separation of the complexing cation from its counter-anion does not appear to be as much a function of its size compatibility with respect to that of the crown cavity as of, for example, its affinity towards the counter-anion under the conditions of complexation.

(b) The anion effect

The anion effect is all important in as much as the M^{z+}–crown interaction can be influenced as the charge on the chelating system of an anion is gradually delocalized. Thus, from the $Mg(onp)_2$–B15C5 and $Ca(onp)_2$–B15C5 reaction mixtures, the salts are recovered uncomplexed while the corresponding salts of the comparatively charge-delocalized dnp^-, viz. $Mg(dnp)_2$ and $Ca(dnp)_2$, yield defined 1 : 1 complexes irrespective of the nature of the medium [119]. If the salts of the even more delocalized pic^- are used, then on addition of water to the reaction medium (ethanol), the 1 : 2 complex for Ca^{2+} can also be crystallized [117]; it is not yet known whether both the crown molecules sandwich the cation. If, however, the anion effect is drastically reduced during the Ca^{2+}–crown interaction, using picH in the $Ca(pic)_2$–B15C5 reaction mixture (which binds pic^- through homoconjugation), the 1 : 2 complex from ethanol can be obtained without recourse to the use of water. Such a reduction of the anion effect can also be accomplished

by using the reaction mixture $CaCl_2$–B15C5–picH [119]. Herein Ca^{2+}–B15C5 and $Cl^- \cdots$ Hpic interactions take place simultaneously and Ca^{2+} complexation takes place even before the charge neutralizing anion (pic^-), obtained through decomposition of the heteroconjugate ($Cl^- \cdots$ Hpic), approaches the complexed cation. The positive result of reducing the anion effect is also obvious from the following observations.

(i) Whereas a complex of KCl with B15C5 cannot be synthesized as such under any conditions [91,93], those of the type $K(B15C5)_2(Cl,HL)$ [93] can be synthesized in the presence of HL (Honp or Hdnp); such complexes are practically colourless in solution as well as in the solid state because of an effective charge delocalization of HL through formation of the $Cl^- \cdots$ HL conjugate.

(ii) Although synthesis of a complex of $BaBr_2$ with 15C5 from a pure organic medium is not known, a charge-separated complex $[Ba(15C5)_2](Br_2,2H_2O)$ [125] has been crystallized in the presence of water which acts to reduce the effect of the anion.

The chemistry of practically every cation towards a crown can be modified through varying its charge neutralizer. The following observations are important.

(i) Both $CsBPh_4$ [94] and $CsClO_4$ [143] yield a 1 : 2 complex with B15C5, whereas for Cs(pic) the anion exercises a strong effect on the poorly polarizing cation and thereby restricts the cation–crown interaction to 1 : 1 [144] (X-ray analysis, Fig. 13).

(ii) KNCS can be charge separated [153] through effective complexation with 18C6 while K_2MoO_4 only partially so [187]. The poorly basic DB18C6 as such fails to charge separate K^+ even from I^- but in a state co-ligated by one molecule of water it does (K^+–I^-, 6.16 Å) [155]; the water molecule also holds the anion. In the system KI(DB18C6) · thiourea [173], bonding of I^- with thiourea occurs and the K^+–I^- distance is rather long; the complex is still ion-paired which can be attributed to the poor proton-donating ability of thiourea. The K^+–S(thiourea) interaction does not show the effect of K^+–O(water) co-ligation because of a poor donor atom preference of K^+ for S. Anion stabilization, therefore, is a function of the original cation–anion pair strength, cation stabilization with the complexing crown, and double action of the added proton donor.

(iii) B15C5 yields no solid complex with NaCl (or NaOH) from polar organic media [91] because of an unsurmountable involvement of the cation with the highly nucleophilic Cl^- (or OH^-)—"total" anion/crown preference. However, NaBr, NaI and NaNCS each yield a 1 : 1 ion-paired complex [91] rather favourably in this order, while for $NaClO_4$ or $NaBPh_4$ the cation can manage its self-encapsulation and can even yield a 1 : 2 charge-separated complex with the same crown [138].

(iv) With B15C5, $Ca(NCS)_2$ yields 1 : 1 complexes under all conditions but $Ca(BPh_4)_2$ yields exclusively a 1 : 2 complex even when the reaction mixture is 1 : 1 [108]. The influence exercised by an anion towards M^{z+}–crown complexation is not just because of its own inherent structural features but also on the electrostatic invitation it receives from the counter-cation. With $Ba(NCS)_2$ [85] and $Ba(ClO_4)_2$ [108], B15C5 yields 1 : 2 complexes, understandably charge-separated sandwich encapsulates, whereas X-ray analysis reveals $Ba(pic)_2(B15C5) \cdot H_2O$ [121] to be only a 1 : 1 ion-paired complex; replacement of pic^- with dnb^- results in the formation of a 2 : 2 ion-paired dimeric complex $[Ba(dnb)_2(B15C5)]_2$ in the crystal lattice [115].

The anion contribution can be permanently recorded in the crystal lattice. For the lower charge density cations, the effect is in general diminished while for the higher charge density ones it is accordingly pronounced in the sense that either the cation is pulled out with respect to the plane of the cavity or the cation encapsulation in the cavity is counteracted. Thus, in the complex [K(18C6)]NCS [153] the anion is in a weakly interacting (disordered) state so that the cation is approximately in the plane of the crown ring whereas the more "cationphilic" eaa^- in the complex K(eaa)(18C6) [172] pulls out the cation from the same donor ring by about 0.9 Å; the higher charge density Na^+ in Na(eaa)(15C5) [167] is pulled out by as much as 1.05 Å despite the fact that this crown could have accommodated Na^+ even more effectively. The cation in $[Na(B15C5)(H_2O)]I$ [128] is pulled out of the plane of the crown ring by only 0.75 Å while the same cation in $Na(dnb)(B15C5) \cdot H_2O$ [169] is pulled to a greater extent (0.90 Å) by the chelating dnb^-. On the other hand, the similar-sized divalent Ca^{2+} in the complex $[Ca(dnb)_2(B15C5)](B15C5,3H_2O)$ [114] is strongly pulled out (1.38 Å) by dnb^-; being a higher charge density cation, Ca^{2+} could have penetrated more effectively into the cavity of the crown. With the same crown, $Ca(NCS)_2$ yields $Ca(NCS)_2(B15C5)$ in the anhydrous state or in a state solvated with water or methanol [108,110] (wherein the cation is, of course, complexed with the crown) but in the product $[Ca(pic)_2(H_2O)_3]B15C5$ [190] the cation is involved only within the solvent and the anionic environment.

Interestingly, the effect of the anion on bonding behaviour and conformation of a crown may be recorded permanently even if the anion is ultimately separated from the complexed cation as may be expected for a sandwich. Such a conformation effect, which an anion can exercise during complexation, has been noted for Na^+–B15C5 sandwiches when ClO_4^- is replaced with BPh_4^- [138] and for K^+–B15C5 sandwiches when I^- [129] is replaced with pic^- [130] or the homoconjugate $(dnb \cdot 2Hdnb)^-$ [131].

If the anion is chelating as well as bulky, it may dictate the M^{z+}–crown complexation so that both bonding behaviour and conformation of the

crown are modified. In the complex $Ba(pic)_2(DB24C8) \cdot 2H_2O$ [118], for example, the pic^- anions neither permit the formation of a 2 : 1 bimetallic complex (as is possible for the similar-sized K^+ with this crown [177,178]) nor do they allow a wrap-around of the crown to be seen with the same cation and the same crown in the complex $Ba(ClO_4)_2(DB24C8)$ [112].

The anion may even alter cation discrimination patterns by the crown. Irrespective of the reaction conditions, Rb(pic) [145] and Cs(pic) [144] form isomorphous 1 : 1 complexes while K(pic) yields a completely charge-separated 1 : 2 sandwich [130]. Obviously, therefore, it is because of pic^- that Rb^+ gets grouped with Cs^+ although under most conditions Rb^+ mimics K^+ [175].

We are satisfied to note that the concept of the anion effect, upon which we commented quite early [9,11,91], is now catching increasing attention [163].

(c) The crown contribution

The very fact that a vast number of M^{z+}–crown complexes have been obtained shows that there is something special about such MCM complexation, namely the multichelating nature of MCM and the macrocyclic effect associated with their chelation. Under favourable conditions with respect to the anionic species, the rather small cavity (powerful) crowns such as 12C4 and 15C5 tend to cause charge separation of the low charge density cations (ligand encapsulation) as well as of the higher charge density ones (self-encapsulation). However, a multidentate of a high order such as DB30C10, which by implication has a large cavity, can successfully cause charge separation of a low charge density cation (K^+, Rb^+ or Cs^+) but may yield to a higher charge density cation which interacts strongly with its counter-anion. Thus, while complexes such as [K(DB30C10)]I [147], [K(DB30C10)]NCS [148] and $[Rb(DB30C10)]NCS \cdot H_2O$ [149] are characterized through X-ray analysis to be genuine charge-separated wrap-around encapsulates, Na^+ usually dictates the formation of anion-paired bimetallic species such as $(NaI)_2(DB30C10)$ [90] and $(NaNCS)_2(DB30C10)$ [176]. The behaviour such as the one towards Na^+ may be rather general for any anion-involved cation for which the cation–crown interaction energy fails to offset the conformational energy required for wrap-around encapsulation; asymmetric aromatic fusion on the crown ring may, however, help to overcome the situation as noted from the formation of the charge-separated complex [Na(*asym*-DB24C8)]ClO_4 [150] compared with the NaX–DB24C8 systems.

For a medium size crown such as 18C6 and especially the less basic DB18C6, charge separation may be practically impossible (except perhaps for Rb^+ and Cs^+ under certain conditions) for the anionic competitors

successfully "sense" the complexed cation from either axial direction and ultimately pair with it yielding anion-paired 1 : 1 complexes, in general.

(d) The role of solvent

The all important role of water towards the synthesiś of complexes has been highlighted in Section B (i) and Section B (iii) (b), in the latter with special reference to anion stabilization. The role of solvents other than water can, sometimes, be dramatic. Thus, reaction of the $KNCS–Ca(NCS)_2$ mixture [108] with B15C5 in ethyl acetate yields $Ca(NCS)_2(B15C5) \cdot H_2O$ whereas the same mixture in methanol yields $KNCS(B15C5)_2 \cdot MeOH$. Formation of M^{z+}–crown complexes containing one or more molecules of solvent is not uncommon. Incorporation of the solvent in the solid lattice is not always a requirement, but is also due to chance availability. Thus, in addition to the complexes $Ca(NCS)_2(B15C5) \cdot MeOH$ [110] and $Ca(NCS)_2(B15C5) \cdot H_2O$ [110] the corresponding anhydrous complex is also known [108].

The role of water in the lattice can, however, be all important. Using X-ray analysis it is clear that in $[Mg(H_2O)_6](12C4)Cl_2$ [189] and $[Ca(12C4)(H_2O)_4](Cl_2,4H_2O)$ [124] the cation-coordinated molecules of water serve to keep the Cl^- ions off the cation and in the case of the Mg^{2+} product also in crown molecule. Also in the complex $[Ba(15C5)_2](Br_2,2H_2O)$ [125], charge separation of the cation may be related to the bonding of water molecules with the Br^- ions (in addition to the self-encapsulating ability of Ba^{2+} towards the crown).

A molecule of water may simultaneously be required to satisfy the coordinative requirements of two cations present in the lattice or for the structural stabilization of the complex moieties therein. This rather uncommon phenomenon is exhibited by (i) the so-called bimetallic complex $(LiNCS)_2(18C6) \cdot 2H_2O$ [151] wherein the water molecule coordinated to the NCS^--paired Li^+ is also coordinated to the other Li^+ not paired with NCS^-, (ii) the complex $NaBr(DB18C6) \cdot 2H_2O$ [156] wherein one of the two water molecules functions as a link between the two moieties $[Na(DB18C6)(H_2O)_2]Br$ and $[NaBr(DB18C6)(H_2O)]$, and (iii) the 2 : 2 ion-paired complex $K_2(Mo_6O_{19})(18C6)_2(H_2O)$ [186] wherein, too, the water molecule is coordinated to both the cations.

(iv) M^{z+}–crown complexation in solution—general

Solution studies on the M^{z+}–crown systems have been carried out from the following viewpoints:

(a) To detect complexation and determine the equilibrium constants [72,92,101,102,142,191–259] for the M^{z+}–crown systems.

(b) To investigate the structure of M^{z+}–crown complexes in solution, essentially the nature of ion pairs [167,196,217,218,220,221,225,227,251,260–276].

(c) To study conformation changes of a crown on complexation with M^{z+} [89,225,277–282].

(d) To determine the rate constants for understanding the M^{z+}–crown interaction mechanism [219,246,283–295].

(e) To investigate the role of crowns as lipophilizing (solubilizing) agents for the M^{z+}–salts [10,40,48,58,141,259] and as ionophores towards phase transfer of M^{z+} from an aqueous to a non-polar organic phase [113,210,259,296–344] as well as towards transport of M^{z+} from an aqueous to another aqueous phase across a non-polar bulk membrane [299,345–371].

(f) To investigate miscellaneous aspects of M^{z+}–crown interaction such as thermodynamic parameters of the transfer from water to a non-aqueous solvent [372–375] and the nature of M^{z+}–crown bonds and M^{z+}–crown encagement forces [376,377]. Other studies include complexation comparison using say ^{1}H NMR [282,378] and volume or compressibility changes [379], and studies such as exploration of the possibility of the use of ^{17}O NMR [380] and ^{87}Rb NMR [381]; fluorescent enhancement of a crown by M^{+} [382] and relative basicity of the different crown ring oxygens [383] using ^{1}H NMR are included in the examination.

(v) Equilibrium constant studies

The most widely spread and intensive of the solution studies are those concerning equilibrium constant determination. These are executed with the aim of studying the factors relating to the selectivity of complexation as a function of the cation, crown, solvent and (occasionally) the counter-anion; variation in the nature of the crown includes change in the cavity size, the number of donor oxygens, and the substituents on the donor ring. The techniques of study have been conductometry [191–203], potentiometry [92,101,102,142,195,204–216,250], UV spectrophotometry [217–224], ^{1}H NMR [225–227,259], ^{13}C NMR [228–231], M^{+} NMR [228,229,232–240], calorimetry [72,241–246] and polarography [247–250]. Other methods such as electric dipole moment measurements [251], circular dichroism [252], electrochemical double-cell method (without liquid junction) [253], potentiometry using cation exchange membrane [254], solubility measurements [208,214,215], ebulliometry [255,256] and the recently developed fast atom bombardment (FAB) mass spectrometry [257,258], have also been utilized.

The broad principles were in fact laid down by the very early spectrophotometric results of Wong et al. [217], the potentiometric work by Frensdorff [142], and calorimetric work by Izatt et al. [241]. These workers incorporated

the cation–cavity size relationship, the nature of substituents of the crown ring and the effect of the solvent on the stability of the M^{z+}–crown complexes. With regard to the techniques adopted for the equilibrium studies, further avenues were opened by the conductometric work of Evans et al. [191] and of Shchori and Jagur-Grodzinski [192], the polarographic work of Koryta and Mittal [247] and the M^+ NMR work of Mei et al. [232].

The overall crown-wise results for 12C4 [196,210,213,216,231,236,250,254–256,258], tetramethyl-12-crown-4 (TM12C4) [196], DB14C4 [217], dicyclohexano-14-crown-4 (DC14C4) [142], 15C5 [196,197,207,209,210,212,216,228,229,236,242,245,254,256,258], B15C5 [200,204,220,227–229,243], methylbenzo-15-crown-5 (MB15C5) [218], *t*-butylbenzo-15-crown-5 (BB15C5) [213], benzodimethyl-15-crown-5 (BDM15C5) [252], dibenzo-15-crown-5 (DB15C5) [102], dibenzodimethyl-15-crown-5 (DBDM15C5) [102], cyclohexano-15-crown-5 (C15C5) [142,251], 18C6 [72,142,196,197,199,200,206,207,209,211,212,216,228,229,232,233,236,238–240,242,243,245,246,254–258], B18C6 [92,220,223–225,249], methylbenzo-18-crown-6 (MB18C6) [218], DB18C6 [142,191–194,201,202,204,208,212,220,222,225,233,251,258], dimethyldibenzo-18-crown-6 (DMDB18C6) [217,249], di-*t*-butyldibenzo-18-crown-6 (DBDB18C6) [195,213,215], tetra-*t*-butyldibenzo-18-crown-6 (TBDB18C6) [195], dibenzodimethyl-18-crown-6 (DBDM18C6) [102], cyclohexano-18-crown-6 (C18C6) [142], DC18C6 [142,191,204,205,233,241,247,248,253,257,258], 21-crown-7 (21C7) [142,216,245], dibenzo-21-crown-7 (DB21C7) [142,230,237], dicyclohexano-21-crown-7 (DC21C7) [142], 24-crown-8 (24C8) [142,216], DB24C8 [101,142,197,198,203,230,235,237,242,243], dimethyldibenzo-24-crown-8 (DMDB24C8) [249], dicyclohexano-24-crown-8 (DC24C8) [142,258], *asym*-DB24C8 [101], dibenzo-27-crown-9 (DB27C9) [230,235,237,243], DB30C10 [92,142,204,213,214,219,225,234,249] and dimethyldibenzo-30-crown-10 (DMDB30C10) [92,249] may be located as indicated.

The results of studies on a particular single M^{z+} with a variety of MCM are of little use in the present context and hence excluded from tabulation in this article. The results of a macrocycle with a variety of cations are of relevance and the recent results with crowns are indexed in Table 2; previous results may be traced in earlier reviews [52,53,691].

We illustrate below that basic results arising from the cation–cavity compatibility are strongly influenced by the polarizability (ligand encapsulation) or polarizing ability (self-encapsulation) of the cation with respect to the donor oxygens, the anion effect of the counter-anion, the diverse effects of the solvent (with respect to the cation, anion and crown), and by the presence of substituents on the donor ring.

(a) The crown contribution

When the anion and solvent effects are not strong, the cation–cavity size

TABLE 2

Recent results on the stability constants of diverse M^{z+}–crown complexes under different conditions [a]

Ligand	Method [b]	Experimental conditions			Stability unit	Cation									Ref.
		Medium	Temperature (°C)	Counter-anion [c]		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	
12C4	CON	MeCN,	25,	I^- (Li^+), BPh_4^- (Na^+)	K	2523	2072								196
	POT	MeOH,	25,	Cl^-	$\log K_1$		1.41	1.58							210
					$\log K_2$		2.20	0.15							
	POT	PC,	25,	ClO_4^-	$\log \beta_1$						2.61	5.53	5.29	4.63	213
					$\log \beta_2$						6.2	9.51	7.91	7.9	
	POT	MeOH,	25,	Cl^-	$\log K$		1.7	1.74							216
	^{13}C NMR	MeOH,	30,	ClO_4^- (Li^+, Na^+)	$\log K_1$	<1 [d]	2.1	1.7							231
				I^- (K^+)	$\log K_2$		3.8	2.4							
	POT	PC,	25,	ClO_4^-	$\log \beta_1$	2.93	3.5								250
					$\log \beta_2$		6.31								
	POL	PC,	25,	ClO_4^-	$\log \beta_1$		3.6	2.15	1.69	1.43					250
					$\log \beta_2$		6.17								
15C5	CON	MeCN,	25,	I^- (Li^+) BPh_4^- (Na^+, K^+)	K	[e]	[e]	[e]							196
	CON	PC,	25,	ClO_4^-	$\log K$	4.2	3.7	3.4	3.0	2.6					197
	POT	MeOH,	25,	not mentioned	$\log K_1$		3.3	3.3							207
	POT	MeOH,	25,	Cl^-	$\log K_1$		3.30	3.34							210
					$\log K_2$		1.44	2.21							
	POT	MeOH,	25,	Cl^-	$\log K$		3.24	3.43				2.36			216
	CAL	MeOH,	25,	Cl^- (M^+) NO_3^- (Mg^{2+}, Ca^{2+}, Sr^{2+}) ClO_4^- (Ba^{2+})	$\log K$	NMH [f]	3.48	3.77 [g]		2.18	NMH [f]	2.18	2.63 [g]		245
15C5	POT–CEM	H_2O,	25,	Cl^-	K		4.7	5.8		6.2		[h]			254
B15C5	CON	PC,	25,	ClO_4^-	$\log K$	3.7	4.3	2.7	2.3	2.0					200
BB15C5	POT	PC,	25,	ClO_4^-	$\log \beta_1$						6.72	6.05	5.55	5.35	213
					$\log \beta_2$								10.6	10.4	

DB15C5	POT	MeOH,	25,		log K		2.2	2.0							102
					log β_2			5.21							
18C6	CAL	MeOH,	25,	Cl^- (Na^+, K^+) ClO_4^- (Ba^{2+})	log K		4.36	6.06						7.04	72
	CON	PC,	25,	ClO_4^-	log K		5.6	6.2	5.3	4.4					197
	CON	DMF,	25,	ClO_4^-	log K		2.4	4.3	3.9	3.6					199
	POT	MeOH,	25,	not mentioned	log K_1		4.3	6.0							207
	POT	MeCN,	25,	ClO_4^-	log K		4.5	5.7							208
		PC,	25,	pic^-	log K		5.2	6.3		4.5					
		DMSO,	25,	ClO_4^-	log K		1.4	3.2							
	POT	MeOH,	25,	Cl^-	log K		4.35	6.08				3.90			216
	CAL	MeOH,	25,	Cl^- (M^+) NO_3^- (Mg^{2+}, Ca^{2+}, Sr^{2+}) ClO_4^- (Ba^{2+})	log K	NMH [f]	4.36	6.06	5.32	4.79	NMH [f]	3.86	> 5.5	7.04	245
	POT–CEM	H_2O,	25,	Cl^-	K		6.6	111.6		9.6		3.0			254
B18C6	SPEC	MeOH,	25,	Br^-	log K		4.03	5.27	4.62	3.66		3.50	4.92	5.35	223
	SPEC	99 vol.% DMSO –1 vol.% H_2O,	25,	Br^-	log K	[h]	1.70	2.85	2.49	2.25					224
DB18C6	POT	MeCN,	25,	ClO_4^-	log K		4.8	4.8							208
		PC,	25,	pic^-	log K		5.2	5.1	3.9	3.3					
		DMSO,	25,	ClO_4^-	log K		1.9	2.4							
	SM	H_2O,	25,	NO_3^-	log K		1.1	1.6							208
		MeOH,	25,	IO_3^-	log K		4.4	5.0	4.2						
DMDB18C6															
	POT	MeOH,	25,	Cl^-	log K_1		4.32	5.06	4.07	3.54					195
					log K_2					2.88					
	CON	DMSO,	25,	ClO_4^-	log K_1		3.30	3.42	3.35	3.31					195
		MeCN,	25,	BPh_4^-	log K_1		5.08	4.98	4.09	3.37					
	POT	PC,	25,	ClO_4^-	log β_1						<1	6.86	7.82	7.66	213

TABLE 2 (continued)

Ligand	Method [b]	Experimental conditions			Stability unit	Cation									Ref.
		Medium	Temperature (°C)	Counter-anion [c]		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	
TBDB18C6															
	POT	MeOH,	25,	Cl^-	log K_1		2.20	3.20	3.23	3.17					195
	CON	DMSO,	25,	ClO_4^-	log K_1		3.16	3.32	3.30	3.13					195
		MeCN,	25,	BPh_4^-	log K_1		4.21	4.04	4.10	3.43					
21C7	POT	MeOH,	25,	Cl^-	log K		2.54	4.35				2.80			216
	CAL	MeOH,	25,	$Cl^-(M^+)$ $NO_3^-(Mg^{2+}, Ca^{2+}, Sr^{2+})$ $ClO_4^-(Ba^{2+})$	log K	NMH [f]	1.73	4.22	4.86	5.01		[i]	1.77	5.44	245
24C8	POT	MeOH,	25,	Cl^-	log K		2.35	3.53				2.66			216
DB24C8	POT	MeOH,	not mentioned	not mentioned	log K		2.25	3.6	3.85						101
	CON	PC,	25,	ClO_4^-	log K		4.1	3.7	3.5	3.4					197
	CON	MeOH,	25,	ClO_4^-	log K			3.5	3.8	3.8					198
	CON	MeCN,	25,	ClO_4^-	log K		4.1	3.8	3.8	4.0					203
DB30C10	POT	PC,	25,	ClO_4^-	log β_1						2.89	5.23	7.67	9.33	213

[a] The earlier results and also recent results for only a single cation are excluded.

[b] CAL, calorimetry; CON, conductometry; POL, polarography; POT, potentiometry; POT–CEM, potentiometry using cation exchange membrane; SM, solubility measurements; SPEC, spectroscopy.

[c] We feel strongly that the counter-anion should also be specified when mentioning the stability values [9].

[d] Estimated value.

[e] Values of K for Li^+–15C5, Na^+–15C5 and K^+–15C5 complexes are 3984 ± 300, 190563 ± 13000 and 950 ± 500 respectively.

[f] NMH, no measurable heat.

[g] Reaction of stoichiometry other than 1:1 which was not resolved.

[h] No measurable interaction.

[i] Heat produced but insufficient to calculate log K.

compatibility can be the main consideration so that M^{z+}–crown interaction should be most favoured for the best-fit system, e.g., 18C6 is most selective for K^+ and 21C7 for Cs^+ [245]. The next preference of the crown should in principle be for a cation which is larger than its cavity so that the M^{z+}–oxygen contacts become possible without undergoing major conformation changes; the cation should also be polarizable (ligand encapsulation). Despite these conditions, however, the stability of such a complex is, in general, lower than that of the corresponding best-fit system, for the cation remains rather exposed to the solvating and charge neutralizing anionic species. Thus, the 1 : 1 complexes of Rb^+ and Cs^+ with B15C5 in 70 vol.% methanol–30 vol.% water are more stable than that with K^+ [243] yet the stability values are lower than for the best-fit K^+–18C6 system in the same medium.

Complexation with a crown should be rather unfavourable when the cation is smaller than the cavity of the crown because the conformation changes for the crown required to complex a small cation are significant and the cation, too, is strongly involved with the anionic species. Thus, the stabilities of the 21C7 complexes with Cs^+ (log $K = 5.01$, $\Delta H = -11.18$ kcal mol^{-1}), Rb^+ (log $K = 4.86$, $\Delta H = 9.66$ kcal mol^{-1}), K^+ (log $K = 4.22$, $\Delta H = -8.59$ kcal mol^{-1}) and Na^+ (log $K = 1.73$, $\Delta H = -10.37$ kcal mol^{-1}) decrease [245] from the best-fit Cs^+–21C7 to the most loose-fit (entropy destabilized) Na^+–21C7, although the enthalpy of the reaction for Na^+ is fairly high but slightly lower only than that for Cs^+.

Our previous review [9] reflects our early consciousness about such a crown contribution. The present article provides additional support with new results especially those with unsubstituted crowns for which the substitution effects, which make the results ambiguous, are absent.

Irrespective of the cation–cavity size compatibility, the complexing ability of a crown towards a cation tends to increase with the number of the donor sites on the ring provided the advantage associated with the number of donor sites is not overcompensated by factors such as the ring substitutions. Thus, in water [254], Ca^{2+} is neither complexed with a crown of fewer donor oxygens (12C4) nor with a best-fit one (15C5) but for a six-donor site crown (18C6) the stability of the complex is measurable even though the ring size of this ligand is rather large for the cation. Examination of the results for $M(ClO_4)_2$ salts (Table 2) with crowns possessing four, five and six coordinating sites [213] establishes this point further.

For a given donor ring, the M^{z+}–crown interaction is strongly a function of the number and nature of the substituents, for such substituents alter both the basicity of the ring as well as its flexibility. As expected, the complexing ability usually decreases in the following order: unsubstituted ring, alicyclic-fused ring and aromatic-fused ring, as is well known for the

series 18C6, DC18C6 and DB18C6; the log K values for K^+ in methanol are 6.10, 5.38 and 5.00 respectively [142]. The substitution effects are sometimes intriguing, however. Thus, (i) 21C7 is distinctly Cs^+/K^+ selective [142,245] while DB21C7 exhibits, if anything, a marginal K^+/Cs^+ selectivity [142]. (ii) For Na^+, a lower stability with the flexible 18C6 compared to that with DB18C6 is possible [208] which has been noted for the high donicity aprotic dimethyl sulphoxide (DMSO) as well as for the low donicity aprotic acetonitrile (MeCN). (iii) In propylene carbonate (PC), 15C5 shows [197] a marginal Li^+/Na^+ selectivity while B15C5 is detectably Na^+/Li^+ selective [200].

As noted earlier by Izatt et al. [241], different isomers obtained in the case of alicyclic-fused rings show different complexing abilities [205]; of the five possible isomers of DC18C6, the stability values of the M^+ complexes in methanol are higher for *trans–syn–trans* and *cis–syn–cis* than for *trans–anti–trans* and *cis–anti–cis* respectively, and also for *cis–anti–cis* and *cis–syn–cis* than for *trans–anti–trans* and *trans–syn–trans* respectively. Such differences should arise [241] because of the significant difference in the orientation of the cyclohexano nuclei and hence in the solvation and solvent-structure properties of the isomers.

Whereas cation–cavity size compatibility and donor atom number of the ring should in principle be fundamentally important, other factors can indeed be important to the extent that the former two principles may appear undervalued. Furthermore, the former two can also unexpectedly dominate each other. Thus, if the dibenzo-substituted DB24C8 is removed from the list [197] for comparison with the unsubstituted 18C6 and 15C5 (for obvious reasons), then consistently higher $K_{(M^+-\text{crown})}$ values for 18C6 in PC even for the small cations make one believe that the number of donor atom parameter can dominate the cation–cavity size compatibility factor (see also refs. 209, 216 and 229).

As results became increasingly available under diverse experimental conditions, the simple picture based on the ion–cavity radius concept [40,242,243] became increasingly complicated (Table 2) and the concept eventually lost [96,196,197,209,216,250,255,256] its predictive value. The cavity concept may in fact only be valid when an ideally free M^{z+} undergoes complexation with the crown in the "absence" of influencing factors; nevertheless, its validity remains vivid even under the effect of moderately influencing factors [245]. However, one finds in the literature that cations involved in the dominantly covalent systems, for example, have been investigated for complexation with crowns and in the event of unexpected results, it has been found rather convenient to criticize the ion–cavity radius concept [196,255].

No doubt, we do undervalue the cavity concept with regard to the M^{z+}–crown interaction and interaction stoichiometry in the solid state [9,11], but in solution the stability magnitude envisaged with the help of this concept are broadly correct. The tricky variation of the thermodynamic values with respect to the cavity concept and the stability constants for Na^+ and K^+ with regard to 12C4, 15C5 and 18C6 in methanol and water, for example [211], may be related more to the strong proton-donating nature of the solvent towards the rather strongly basic unsubstituted crown than to the failure of the cavity concept towards the M^{z+}–crown complexation. The results of the work on 12C4 with cations of different sizes have been used [250] to undervalue the cavity concept towards the solution stability of complexes. Herein, too, we feel that in a solvent such as PC, every anion (including ClO_4^-) can exercise an anion effect and the cation can hardly display its original Lewis acidity. Lithium *t*-butoxide in *t*-butanol, for example, should behave as an "organic molecule" and does not become an appropriate example to be quoted [255] to undervalue this concept for any crown whatsoever. In view of a distinct covalency in LiI (Fajans' effect), this should be true for LiI in MeCN [196], irrespective of the crown size.

(b) The cation contribution

Apparently, the stability of a complex is a function of M^{z+}–crown, M^{z+}–anion, M^{z+}–solvent, anion–solvent and crown–solvent interactions but in practice these forces overlap each other so that the stability trends for M^+ as well as M^{2+} ions become unpredictable (Table 2). During the early stages of the development of the subject, most workers considered the cation–cavity size compatibility as the main factor. We, too, held [9] (and still hold) its validity but giving simultaneous importance to the inherited crown/anion preference of the cation (determined by its charge density). As increasing variables are introduced, essentially with respect to the anion, solvent and donor number or substituents of the crown, the stability values for the cations of a series may not only be changed but may show antagonizing cross-overs (see Table 2). Through the use of a series of solvents, for example, the ligand nucleophilicity, anion counteractivity and cation complexability are modified differently for different solvents and one may not know which dominates the other two.

Obviously, therefore, the interactive characteristics of different M^{z+} (which in the present context is the main question of interest) cannot be uncovered and rationalized until the equilibrium constants for a given crown are determined for each selected anion using appropriately selected solvents and for a selected solvent using a representative set of anions. We maintain that the polarizability of the cation by the crown (ligand encapsulation) and

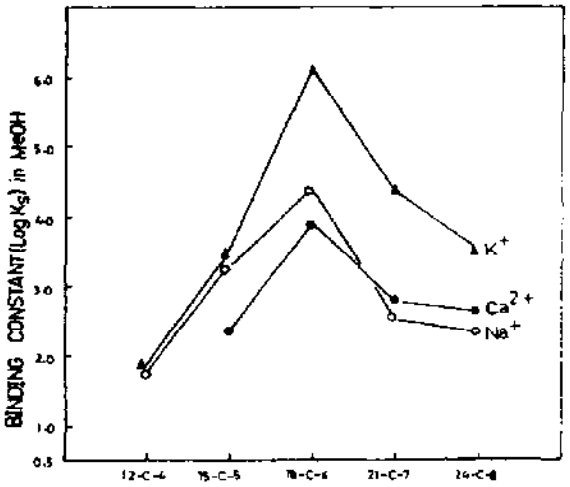


Fig. 19. The relative selectivities of complexation of K^+ and of 18C6 in methanol.

polarizing ability of the cation towards the donor atoms (self-encapsulation) are recognizable factors which contribute to the overall stability value.

Ligand encapsulation is favoured not only when a large (polarizable) cation is involved but apparently also as the cavity size of the complexing crown approaches the cation size. Thus, of Na^+, K^+ and Ca^{2+}, it is the most highly ligand-encapsulated K^+ which is selectively complexed [216] irrespective of the crown (12C4, 15C5, 18C6, 21C7 and 24C8); it is also understandable that the most strongly complexing is the best cavity fit 18C6 (Fig. 19) while the counteracting effect of the strongly nucleophilic Cl^- present in the environment appears to have been minimized by the protic methanol [216]. Also, the enthalpy of formation of the best-fit Cs^+–21C7 in methanol (-11.18 kcal mol^{-1}) is greater [245] than that of the other ligand-encapsulated Rb^+ (-9.66 kcal mol^{-1}) and K^+ (-8.59 kcal mol^{-1}) or that of the self-encapsulating Na^+ (-10.37 kcal mol^{-1}).

A higher charge density cation, which is more a self-encapsulating cation, has by implication also to be anionphilic. Thus, Mg^{2+} and Ca^{2+} do not appear to self-encapsulate into DC18C6 in aqueous medium more effectively than the similar-sized Li^+ and Na^+ respectively, and are therefore poorly complexed [241]. The effect related to anionphilicity is expected to become dominant as (other conditions remaining unchanged) the cavity of the complexing crown becomes large. Both these points are supported by the observation that the enthalpy of the Na^+–21C7 reaction in methanol is very high but in the analogous reaction involving the similar-sized Ca^{2+} insufficient heat is produced to enable calculation of the enthalpy value, although for the larger (less anionphilic) congeners Sr^{2+} and Ba^{2+} the enthalpies are fairly high (-7.10 kcal mol^{-1} and -6.81 kcal mol^{-1} respectively) [245].

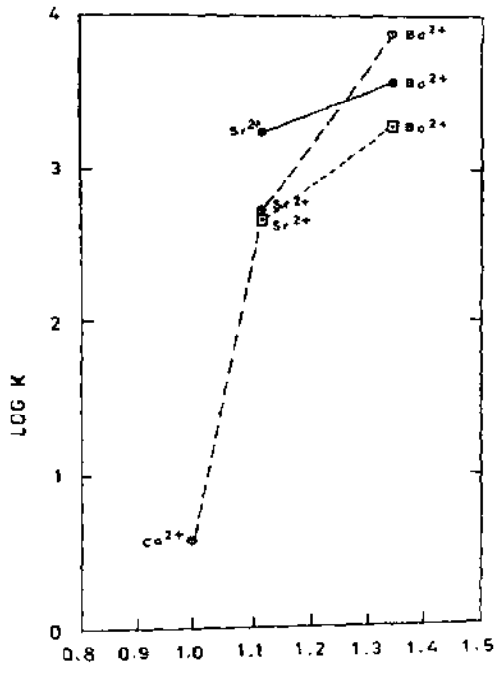


Fig. 20. The gradation in stability of the Ca^{2+}, Sr^{2+} and Ba^{2+} complexes with 18C6 (⊙) and DC18C6 *cis–syn–cis* (●) and DC18C6 *cis–anti–cis* (⊡) in water.

Even the earlier far-IR spectral studies have shown [377] that a lower stability of the Na^+–DB18C6 system than that of the analogous K^+ system relates not to the cation–crown encagement forces but to the enhanced involvement of Na^+ with the anionic species.

Although, complexation of M^{2+} ions with crowns has been less studied and the complexation principles are much less rationalized, some comments are possible. The interaction of M^{2+} with a crown vs. that with the anionic species changes rather abruptly; this abruptness is a function of the solvent as noted for PC [213]. The behaviour of M^{2+} ions is a function of their higher charge density which makes them behave either strongly anionphilic or strongly complexing depending upon the nucleophilicity of the counter-anion, solvating ability of the solvent medium towards the involved ions, and those structural features of the crown which are related to its complexing property. With various crowns the stability values in water decrease in the order Ba^{2+} to Ca^{2+} (see Fig. 20) particularly when the polarity of the medium is reduced through the addition of methanol [242,243]. The overall conclusion is that the M^{2+}–crown complexation of especially the small cations is counteracted by the counter-anion as the cavity of the crown

exceeds the cation size and as, in conjunction with it, a medium of low polarity is used because both these conditions favour an anion over crown preference for the cation. See, however, ref. 213 to note that for a poorly counteracting anion such as ClO_4^-, the low polarity of the solvent favours M^{2+}–crown complexation even for the large-cavity crowns.

The M^{z+}–crown interaction stoichiometry in solution is more sensitive towards the environment than in the solid state, which means that crown/anion preferences of a cation are less defined in solution. Although it is determined by the amount of the crown with respect to the cation, in addition to that of the anionic species, the nature of the cation is vital. Thus, a particular cation (Na^+) compared with others (K^+ and Cs^+) may display [234] a more extended variety of interaction stoichiometries towards, for example, DB30C10 depending upon the solvent used. Even for a low charge density cation like Cs^+ a 1 : 1 complex can be converted into a 1 : 2 complex in a weakly solvating solvent upon the addition of excess crown (18C6), the enthalpy and entropy terms of which determine the magnitude of log K_2 with respect to log K_1 [240].

(c) The anion, solvent and anion–solvent effects

The anion effect is more important for the higher charge density cations but it is not absent even for the low charge density ones including Cs^+. Thus, in methylamine, the equilibrium constants of Cs^+ with 18C6 increase in the order $NCS^- < I^- < BPh_4^-$ [239] reflecting an enhancement in the solution stability in accordance with an increasingly weak competitive effect of the anion. We have been constantly emphasizing in our publications that the M^{z+}–ligand complexation is greatly a function of the nature of the counter-anion. In fact, the key to the regulation of the M^{z+}–ligand complexation is the nucleophilic counteractivity of the counter-anion and there should be no surprise if a change of anion may lead to reversal of selectivity. Obviously, therefore, the solution stability sequences for M^+ and M^{2+} series involving the inconsistent use of anions have no meaning in connection with the precise understanding of the interactivity of different M^{z+}. Although 1 : 2 complexation (sandwich encapsulation) implies charge separation [225,232,233], it has recently been shown by Khazaeli et al. [240] that the anion effect is not ruled out even for the 1 : 2 complexes of the low charge density Cs^+.

The effect of solvent on solution stability is more widely studied and acclaimed than the anion effect which has become prominent only recently; several reviews [52,58,384] deal with the solvent effect in some detail. It is a common recognition that the stability of a complex decreases as a solvent of increasing solvating ability is used; the solvating ability is generally considered to be satisfactorily represented in terms of the Gutmann donor number

(GDN) [385]. A gradually increasing proportion of water in the methanol–water system leads to a consistent decrease in the stability values for Na^+–15C5 and Na^+–18C6 [209] complexes. Interestingly, the solvent effect of solvents of diverse GDN values depends, in turn, on the nature of the complexing cation. Thus, while the stability values of Li^+–crown complexes are strongly dependent on the nature of the solvent [236], those of the systems involving the low charge density and rather weakly solvating Cs^+ are only marginally solvent dependent [234].

Intriguingly, the solvent also modifies the M^{z+}–crown interaction stoichiometry. Thus, for the cation–cavity compatible Li^+–12C4 system the common interaction stoichiometry is 1 : 1 but in nitromethane 1 : 2 complexation has also been noted to take place [236] (cf. ref. 259). Furthermore, while each of Na^+–DB30C10, K^+–DB30C10 and Cs^+–DB30C10 complexes shows, in general, a 1 : 1 (seemingly wrap-around) complexation, the Na^+–DB30C10 complexation in acetone and nitromethane is 2 : 1, 3 : 2 as well as 1 : 1 [234].

The role of solvent is also indirectly important from the viewpoint of its control on the anion effect; in methanol the solution stability of Na^+–TBDB18C6 complex is practically unaffected for a variety of competitive anions, viz. chloride (log $K_1 = 2.60$), bromide (2.66), acetate (2.55), thiocyanate (2.64) and picrate (2.63) [195]. This points to the fact that a protic solvent helps the complexing cation to become rather indifferent to the counter-anion.

The solvent may also influence the stability of a crown complex through solvation of the ligand. Although the crown-solvation aspect has not yet become as widely acclaimed as it should be, it does have an interesting history of development. In 1974, Hinz and Margerum [67] stressed the importance of ligand solvation with regard to the macrocyclic effect and in the same year Gokel et al. [386] reported a stable 18C6–MeCN solid complex. In 1976, Agostiano et al. [248] considered the interaction between the crown and the solvent to be operative before as well as after the inclusion of the cation in the crown cavity. According to these workers, M^{z+} and the crown must undergo desolvation prior to complexation for which an amount of energy equal to $G_{\text{ion-solvent}}$ and $G_{\text{crown-solvent}}$ respectively must be supplied. These workers contended that crown solvation is operative not only for water but also for the alcoholic solvents (see also Hilliard et al. [272] who have used the crown-solvation aspect). de Jong et al. (1976) [387] reported crowns as efficient agents for solubilizing water in chloroform in the absence of any salt. Iwachido et al. (1976) [388] determined the number of water molecules interacting with the uncomplexed DB18C6 to be 0.7. This information attracted the attention of Kolthoff and Chantooni [208] in their studies on M^+–DB18C6 transfer activity coefficients in various solvents.

Live and Chan (1976) [225] postulated the role of water interaction in the context of the crown conformational aspects.

In 1979, we discussed [9] the basic importance of the crown-solvation factor towards M^{z+}–crown complexation. In 1980, Popov and coworkers [236,237] pointed out that crown solvation affects the extent of a complexation reaction and that crown solvation can alter the M^{z+}–crown stability order. In 1982, Hilliard et al. [272] postulated the predominance of the crown–water interaction on the basis of spectral analysis. Gold and Rice (1982) reported [389] the formation constant and stoichiometry of the 18C6–MeCN complex by NMR, Raman and IR spectroscopy. Elbasyouny et al. (1983) [390] explored the field in detail. The overall conclusion is that crown solvation is possible not only for water and other protic solvents but also for the aprotic solvents such as MeCN and that while considering the possible factors affecting the M^{z+}–crown solution stability, crown solvation is a potential factor.

(vi) Ion pair studies

Interest in the study of the nature of anion–cation pairing through cation complexation with crowns began in 1970 [217], although the studies almost exclusively concerned the M^+ ions. The techniques of study include UV spectrophotometry [217,218,220,221,260], ^{23}Na NMR [261], ^{19}F NMR [273], solution IR [167,262,272], Raman spectroscopy [262,272], ESR [265–267,276] for radical anions such as tetracyanoethylene ($tcne^-$), circular dichroism [268,269,275], pulse radiolysis [263], electrical dipole measurements [251] and temperature-dependent fluorescence spectroscopy [270].

It is obvious that the anion–cation interaction weakens on complexation of the cation with a ligand, in particular an MCM; the K^+tos^- distance in octanoic acid [251] is increased through complexation of K^+ with C15C5 and DB18C6 by 0.15 Å and 0.5 Å respectively, compared with that found for the uncomplexed K^+tos^- ion pair. Broadly, two types of ion pairs are recognized: ligand-complexed contact ion pairs and ligand-separated ion pairs. The actual type depends not only on the nature of the cation but also on the pairing ability of the counter-anion, complexing ability (ion pair separating ability) of the crown and solvating ability of the solvent. The following observations are pertinent.

(i) For the size-compatible MB15C5 in ethereal solvents, the higher charge density (anionphilic) Na^+ forms [218] crown-complexed contact ion pairs (in addition to the crown-separated ones) even for the charge-delocalized carbanion, fl^-; of course, the proportion of the crown-separated ion pairs becomes higher in more polar solvents. However, only the crown-separated ion pairs are obtained for the same cation–anion combination even in

ethereal solvents if instead of MB15C5, a crown possessing more coordinating sites, viz. MB18C6, DB18C6 or DC18C6 is employed [217]; in the presence of a chelating anion such as eaa^-, even 18C6 fails to separate the ion pair of Na^+ [261]. Using excess of crown, of course, formation of crown-separated ion pairs is also expected, as noted for 15C5 with Na^+eaa^- [167].

(ii) For $Ba(fl)_2$ in tetrahydrofuran (THF), B15C5 yields a 1 : 2 anion-separated species [220] whereas for $Ba(NCS)_2$ in $CDCl_3$ or CD_3CN, the same crown yields a 1 : 1 complex [227] understandably a contact ion pair which is in contrast to the synthesis of a 1 : 2 complex from methanol, viz. $Ba(NCS)_2(B15C5)_2$ [85] in the solid state.

(iii) K^+, which can be ligand encapsulated, exhibits its inherited tendency of forming crown-separated ion pairs with B15C5 [227] or MB15C5 [218] irrespective of whether the anion is fl^- or NCS^-. However, for the larger-cavity crowns MB18C6 or DC18C6, which permit anion pairing from the axial sides, the same cation appears forced to yield a contact ion pair for a delocalized anion such as fl^- [218] as well as for the highly nucleophilic spherical anions such as F^- [273] or Cl^- [271] even with the unsubstituted 18C6. In the presence of an anion-stabilizing protic solvent such as *t*-butanol, a chelating anion such as eaa^- can be made to adopt a non-chelating "transoid" conformation yielding crown-separated ion pairs as noted for the K^+–18C6 system [264].

Temperature-dependent fluorescence spectroscopy has revealed that in the first excited singlet state (S_1) the π bond of the Na^+–indolyl$^-$ ion pair is converted to a σ bond upon complexation with 18C6 in 2-methyltetrahydrofuran [270]. The Na^+–18C6 interaction appears to have loosened Na^+–indolyl$^-$ pairing which enabled the anion to adopt a more suitable state of interaction.

(vii) Kinetic studies

Early kinetic studies (up to 1977) were reviewed by Liesegang and Eyring [50] providing sizable data on the M^{z+}–crown systems. The techniques adopted for the studies have been T-jump [219], ultrasonic absorption [246,286–289,291,292], M^+ NMR [283–285,294], ^{43}Ca NMR [290], and even the conventional stopped-flow method [293]. The stopped-flow method has been used for a system displaying a low rate of complexation as, for example, with the divalent Sr^{2+} and the rather rigid DB18C6 at low temperature.

Regarding the M^{z+}–MCM complexation mechanism, two main schemes have been proposed. The so-called Chock mechanism [219] envisages first a fast conformational change of the crown and then the reaction of the

appropriate conformation with the cation. The second mechanism is the so-called Eigen valinomycin mechanism [391] wherein formation of the $M^{z+} \cdots$ ligand encounter complex is the first step while desolvation and ligand rearrangement step leads to the final complex. The second step of each mechanism, viz. the complexation step of the Chock mechanism and the desolvation–ligand rearrangement step of the Eigen mechanism, is the rate-determining step. It is, however, being realized that both the schemes are oversimplifications of the actual mechanism.

The Chock mechanism originated from the kinetic studies performed on M^+ with DB30C10 in methanol [219]. Subsequent results [284–289] were also interpreted with its help. During their initial studies on the kinetics of complexation of 18C6 with $LiClO_4$ in 1,3-dioxolane and 1,2-dimethoxyethane (DME), Farber and Petrucci [291] found that their data were amenable to interpretation by both the Chock and Eigen mechanisms. However, later in the same work they obtained evidence for isomeric relaxation of 18C6 in 1,3-dioxolane which appears to provide marginal support to Chock's mechanism, at least with regard to the existence of two forms of the crown. Chen and Petrucci in a subsequent study, interpreted [292] the complexation results of Li^+, Na^+ and K^+ with 18C6 in methanol in terms of the Eigen–valinomycin mechanism, although in their studies the concentration of the complex was so high as to make the encounter step irrelevant. Studies on complexation of 18C6 with Li^+ and Na^+ in dimethylformamide (DMF) or ethanol [246] also provide support to the Eigen mechanism.

Ultrasonic absorption studies on 18C6 for M^+ and Ca^{2+} by the Eyring group revealed [287] complexation constants to be in the order $Ca^{2+} \sim Li^+ < Na^+ < K^+ \sim Cs^+ \sim Rb^+$. This suggests that discrimination of the first three higher charge density cations from the later three low charge density ones originates from the charge density differences of the cation rather than from the cation–cavity size factor. Another vital conclusion of the kinetic work is that the kinetic specificity is more a function of the decomplexation step than of those preceding it in the process. This also means that the consequence of the cation–anion and cation–solvent interactions (which can be related to the decomplexation aspect, too) can be all important even after M^{z+}–crown complexation has taken place. The decomplexation step appears favoured in particular when the cavity of the complexed crown is rigid and strained; compared with 18C6, for instance, 15C5 displays a poor cation selectivity [242] as well as a lack of differentiating pattern in the decomplexation rate constants [288].

For the Na^+–18C6 system in THF or 1,3-dioxolane which contained an excess of Na^+ salt the cation exchange has been found [229] to be slow for BPh_4^- and fast for I^- or ClO_4^-. This is perhaps because with BPh_4^-

solvent-separated ion pairs are formed while for I^- and ClO_4^- they are contact ion pairs. Through ^{23}Na NMR studies on the kinetics of complexation of DB18C6 with Na^+ in DMF, DME and methanol, Shchori and coworkers [283,284] found a minimal influence of the solvent on the activation energy for the decomplexation reaction. Schmidt and Popov [294], however, found a strong solvent dependence of the activation energy: 9.2 kcal mol^{-1} for acetone and methanol, 13.8 kcal mol^{-1} for 80 vol.% acetone–20 vol.% dioxane and 16.8 kcal mol^{-1} for 1,3-dioxolane. The solvent effect can be drastic to the extent that, in addition to the activation energy, even the mechanism could be affected. In contrast to the previous results in aqueous solutions, the cation exchange during $K^+ - 18C6$ complexation in 1,3-dioxolane [294] has been found to proceed via the following bimolecular exchange mechanism

$$*K^+ + K^+ \cdot 18C6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} *K^+ \cdot 18C6 + K^+$$

instead of the dissociative one

$$K^+ + 18C6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} K^+ \cdot 18C6$$

The solvent may affect the number of observable steps during the complexation process which may be related to its solvating ability towards the cation concerned [246].

(viii) Lipophilization, extraction and transport studies

Incorporation of an M^{z+} salt in a non-polar organic phase, as induced by a crown, can be carried out in three ways: (i) dissolution of the salt employing just the organic phase containing a crown (lipophilization); (ii) transfer of the salt dissolved in water into the immiscible organic phase which contains the crown as a phase transfer agent (two-phase transfer, i.e. extraction); (iii) transfer of the salt from an aqueous to another aqueous phase across a layer of a water-immiscible organic phase (three-phase extraction–de-extraction, i.e. transport).

(a) Lipophilization

Lipophilization of an M^{z+} salt in a non-polar medium by a crown is possible because the crown not only diminishes the charge on the cation but also offers a hydrophobic exterior. The lipophilization technique offers a convenient way of evaluating the complexing efficiency of a series of cations towards a ligand in the absence of a polar solvent; ion solvation does not take place and the M^{z+}–crown complexing behaviour under the isolated

effect of the anion is manifest. Unfortunately, however, the lipophilization technique has not been used much for this purpose; the M^{z+}(anion)–crown systems in a non-polar phase have been incorporated in organic reaction studies to generate the "naked" anions rather than to understand the coordinative characteristics of M^{z+}. Nevertheless, the following points deserve attention.

Comparison of the lipophilization efficiency of DC18C6 towards KX (X = Cl, Br or I) in several non-polar organic solvents reveals it to be in the order chloroform ≥ methylene chloride ≫ carbon tetrachloride > benzene [40], suggesting that the solvent contribution is not absent. Also, lipophilization of the KX salts increases in the order $Cl^- < Br^- < I^-$ [40]. Work on complexation of B13C4 with Li^+ in benzene has revealed [259] the lipophilization efficiency to lie in the order $OH^- < Cl^- < ClO_4^- \approx NCS^- < pic^-$, suggesting that the choice of the anion matters. Organic anions, in general, enhance lipophilization, while the highly nucleophilic charge neutralizers such as F^- and SO_4^{2-} strongly deter it [40].

Wong et al. noted [299] the dependence of absorption maxima (λ_{max}) of the anion for the M^{z+}(anion)–crown complexes ($M^+ = Na^+$ or K^+) on the nature of the cation in addition to the structure of the crown; replacement of Na^+ by K^+ in the 1 : 1 Na(pic)–15C5 systems in chloroform causes the λ_{max} to shift from 357 to 362 nm [299] while in either case the stoichiometry is 1 : 1 and the cation constitutes a part of the crown-complexed tight ion pair. Thus, the technique permits study of the M^{z+}–anion state of pairing and even the stoichiometry of the M^{z+}–crown interaction. On the addition of excess crown, the 1 : 1 K(pic)–15C5 complex is converted into a 1 : 2 complex showing λ_{max} at 378 nm [299] but the spectrum of the Na(pic)–15C5 complex remains unaffected suggesting an invariant interaction stoichiometry.

Use of the trichloro(ethylene)platinum(II) salts of M^+ enabled Reinhoudt et al. [226] to develop an NMR method for the determination of complexation constants of the M^+–crown systems even in a non-polar solvent such as deuterochloroform; stabilization of the anion, however, appears particularly vital for obtaining quantitative information about lipophilization adopting this approach.

(b) Extraction

Extraction of M^{z+} from an aqueous phase into an organic phase is a direct result of cation–crown interaction. Pedersen [296] himself tested this method for M^+–crown systems and qualitative information could be obtained. Frensdorff [297] extended the approach in an attempt to study the extraction equilibria. Interest in extraction grew faster from 1978 and as a complexation evaluation technique it is now frequently undertaken.

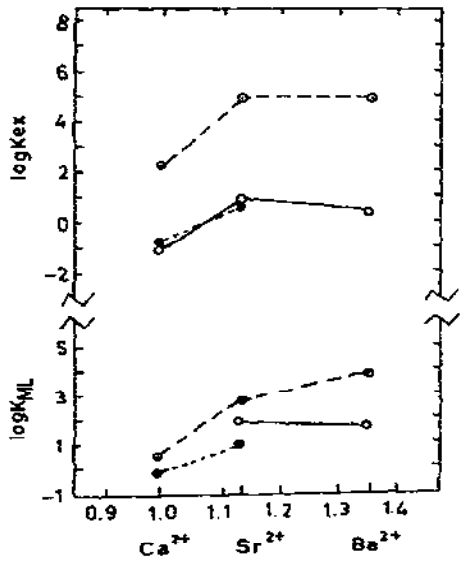


Fig. 21. The extraction efficiency of $M(pic)_2$ from water to benzene with 15C5 (○), 18C6 (⊙) and DB18C6 (●) and its concordance with stability trends of the corresponding systems in water.

Overall examination leads to the conclusion that M^+ has been studied to a much greater extent than M^{2+}. This compares well with the trend of equilibrium constant studies in the homogeneous phase. Large polarizable organic anions such as pic^- and, occasionally, some inorganic anions, in particular, the charge delocalized NO_3^- and NCS^- [259,316,320,330,332] have been used. The free hydration energy of the organic anions is low and can aid extraction of M^{z+} into the organic phase. Anionic azo dyes such as tropeoline 00 and methyl orange [336] have found their use.

The extraction constants (log K_{ext}) for M^{z+}–crown systems, in particular of the 18C6-cavity crowns, have often been found [113,300,301,309,313,320, 324,327] to be in accordance with their solution stability (log K) in homogeneous systems. Figure 21 illustrates extraction of $M(pic)_2$ from water to benzene with 15C5, 18C6 and DB18C6 [312]. It reflects within-the-group selectivities and a qualitative relationship between log K_{ext} trends and the log K [242] trends in aqueous phase; detectable differences in the two being possibly due to the difference in the nature of the anions involved. Because of the concordance of the log K data with the log K_{ext} data, the relevance of the information from the homogeneous systems to the understanding of the cation transport across a lipid membrane becomes apparent.

The structure of the macrocycle is, of course, important with regard to the number of donor atoms as well as the nature and number of substituents.

Whereas a crown such as 12C4 [319] shows no pronounced selectivity for any M^+, perhaps because of a hygroscopic nature and effective crown solvation, 15C5 [313] and 18C6 [313] show the most remarkable selectivity for Na^+ and K^+ respectively. However, 15C5 is not necessarily always Na^+ selective. Using pic^- as the counter-anion, Miyazaki et al. [210] found the extracting power of 15C5 into methylene chloride to be in the order $K^+ > Rb^+ \gg Cs^+ > Na^+ > Li^+$. A large-cavity crown such as DB24C8 shows the highest Ba^{2+}/M^{z+} selectivity [314] but no selectivity amongst M^+ ions.

Substituents incorporated on the crown not only alter the basicity of the ring oxygens but also modify its rigidity and lipophilicity which, in turn, affect the loading capacity of the macrocycle towards M^{z+} into the organic phase. The following observations are illustrative.

(i) Tetraphenyl-18-crown-6 (TP18C6), which carries electron-withdrawing phenyl substituents, displays a weaker extracting power than 18C6 [333] towards M^+ although TP18C6 is more lipophilic than 18C6. This brings forth the electronic effect of the phenyl substituents. TP18C6 is, however, a detectably better extractant than DB18C6 or even tetracyclohexyl-18-crown-6 (TC18C6) [333] which suggests that a contribution of the lipophilic aspect of the crown is there.

(ii) TBDB18C6, wherein four electron-donating *t*-butyl groups are incorporated on the two benzo nuclei of DB18C6, is expected to be a more effective extractant than DB18C6 in view of its obviously greater lipophilicity and perhaps also a better chelating ability. The results with Cs^+ as a test ion [302], however, show that compared with DB18C6, the extracting power of TBDB18C6 is reduced (although slightly) obviously because of the steric effects.

(iii) Incorporation of increasingly bulkier alkyl groups, methyl, ethyl and *n*-butyl on the ring carbon(s) of DB18C6 (rather than on the benzo nuclei) also results in a decrease in the extraction efficiency of the carrier into chloroform [342]. This should also be because of the adverse steric factors.

Although the ion–cavity radius concept should be relevant to the understanding of the extraction results of the M^{z+}–crown systems, unpredicted results can be encountered: for example, (i) for the M^{2+} ions, the log K_{ext} value for Ca^{2+} with 15C5 is the smallest [312] although the crystal radius of Ca^{2+} is nearly equal to the cavity radius of the crown; (ii) the extractability of DB24C8 for M^+ into benzene is not sensitive to the ratio of the ionic size to the cavity size of DB24C8 [311]; and (iii) the size–fit principle is not as consistent for other M^+–crown systems as for K^+–DC18C6 [322] or K^+–18C6 cavity crowns in general. These and other results [210] lead to the conclusion that the chemical restrictions imposed do not permit the size–fit principle to determine the log K_{ext} values (cf. ref. 330).

The interaction stoichiometry of the M^{z+}–crown complex is one of the

main factors which determine the degree of extraction. The enhanced extracting ability of 12C4 towards Na^+ [210] compared with that towards Li^+, for example, is best understood in terms of the 1 : 2 sandwich encapsulation of Na^+ by the crown. With DB18C6, the 1 : 1 complexes of Rb^+ and Cs^+ could be converted to 1 : 2 in the presence of excess crown [300]. By doing this, extraction is also enhanced.

The counter-anion is important for the possibility and extent of extraction. Multiply charged highly nucleophilic anions such as SO_4^{2-} certainly inhibit the process of extraction. Pedersen [296] found that for the K^+–DC18C6 system (i) OH^- and F^- do not allow extraction even with the polar methylene chloride, (ii) MnO_4^- permits with methylene chloride and toluene but not with cyclohexane, while (iii) for pic^- the extraction is possible with all solvents, although to different degrees.

An organic anion such as pic^- is not only a charge-delocalized (less nucleophilic) anion but contributes to the organic character of the M^{z+}(anion)–crown system. However, it appears that there has to be a balance between the hydrophobicity and nucleophilicity. Using pic^- as the counter-anion, solvent extraction into polyurethane foam is possible with DC18C6 for all M^+ except Li^+ [327], whereas using dnp^-, which is obviously more hydrophobic and more nucleophilic than pic^-, no extraction is possible for any M^+ under the same conditions. The use of a more hydrophobic and less nucleophilic anion such as 8-anilino-1-naphthalene sulphonate (ans^-) leads to better extraction even compared with that using pic^-. The choice of the proper counter-anion has an important bearing on the selectivity of the extraction. The selectivity of extraction of K^+ over Na^+ by DC18C6 into methylene chloride, for example, is of the order of 100 for pic^- but only 2 for dipicrylaminate [307].

The anion effect can be vital even if the anion involved is not hydrophobic. Thus, distribution coefficients of M^+ by DC18C6 into dichloroethane (DCE) is in the order $F^- < Cl^- \leqslant OH^- < Br^- < NO_3^- < I^- < ClO_4^-$ [320] which qualitatively corresponds to the decrease in hydration energies of these anions. Some other publications [299,301,303,306,330,332] also reflect the importance of this point. Broadly, anion control on the extraction process has been noted more frequently and confidently than that for the homogeneous systems.

Attention has not been focused on the role of the anion towards the possibility of altering the extraction sequences of M^+ and M^{2+}. The order of extraction of M^+ ions, $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, by DC18C6 into DCE [320], is independent of the inorganic anions used for this work. However, we believe that a more extended study using diverse anions should reveal some interesting cross-overs.

It seems unlikely that variation of the non-polar solvent (referred to as

diluent), can cause drastic differences; nevertheless, the differences can be detected. With NCS^- as the counter-anion, extraction of each of Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} by B13C4, for example, is more effective into methylene chloride than benzene [259]. Intriguingly, however, extraction of Sr^{2+} with DB18C6 is higher for benzene than chloroform [315] even though benzene is a solvent of very low dielectric constant. Extraction of K^+ by 18C6, DB18C6 or DC18C6 into methylene chloride is quantitative [341], whereas it is incomplete for the other diluents such as benzene, toluene and chloroform. The general selectivity sequence for various nitrobenzene–toluene mixtures is independent of the diluent proportions [301]. Use of polyurethane foam instead of a common organic solvent as a diluent [326,327] has provided a novelty in the experimentation of extraction.

There is growing interest in investigating synergistic extraction [322,323,325,329,339] employing a co-extractant in conjunction with the macrocycle. The co-extractant can either be an electrically neutral Lewis base such as tri-octylphosphine oxide or an organic-soluble but water-insoluble cation exchanger such as di(2-ethylhexyl)phosphoric acid. The latter is interesting from the viewpoint of avoiding the problem of a mineral acid anion such as SO_4^{2-} getting solubilized in a non-polar organic diluent.

Extraction of M^{z+} into an organic phase from an aqueous acidic solution, containing the parent acid of the counter-anion, is a new trend [316,332,337]. Nitrate in the presence of HNO_3 has been the anion of choice and extraction of even M^{2+} ions is possible using DC18C6 [337] under a prescribed range of acid concentration. Studies have revealed that for DC18C6, the distribution coefficients of MNO_3 pass through a maximum (at 1.5–2.0 M HNO_3) and then decrease; the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, of course, remains unchanged. Nitric acid should incorporate an equilibrium of the type $HNO_3^* + NO_3^- \rightleftharpoons HNO_3 + NO_3^{*-}$ but the contribution could be more through the salting out effect; an increase in concentration of HNO_3 beyond an optimum value results in decreased extraction understandably because of the lesser availability of the free extractant which is caused by co-extraction of HNO_3 [332]. Incorporation of cyclic voltammetry [340] and the possible use of calorimetry [343] in the two-phase systems have been proposed.

(c) Transport

For a transport process of M^{z+} from an aqueous to another aqueous phase across a non-polar phase, the macrocycle present in the non-polar phase acts as a carrier and the process is termed carrier-mediated or carrier-facilitated transport. Such transport can take place in the direction of the concentration gradient (passive transport) or against it (active transport). For the electrically neutral macrocycles, the transport is, in general, in the

passive mode although under imposed conditions it can be carried out in the active mode.

The significance of ion binding to ion transport was pointed out by Izatt et al. [392]. Except for a few earlier publications [299,345,346] the thrust in these investigations occurred from 1978.

The methodology for model membrane transport has been described in detail [393]. A model membrane is composed of an immiscible non-polar organic phase which defines an interface with the two aqueous phases, namely the source phase and the receiving phase. A membrane can be of the bulk liquid type or the emulsion type. The bulk type is characterized by a lower heavier organic non-polar phase over which are placed the two aqueous phases appropriately separated from each other. An emulsion membrane incorporates the receiving aqueous phase within the non-polar organic phase (also containing a surfactant in addition to the carrier) which, in turn, is surrounded by an external aqueous phase (source phase); an emulsion membrane is, thus, of the pattern water-in-oil-in-water and requires lesser amounts of the solvent and the carrier than needed for a bulk membrane.

The process of facilitated transport involves extraction and de-extraction of M^{z+}. It has been suggested [362] that the rate of transport is determined basically by the rate of release rather than that of the uptake. It has also been emphasized [354] that the results of the transport studies obtained under different conditions (such as stirring rates, transport path lengths and different anions) must not be compared with each other. This point becomes all the more important when comparison of the transport behaviour of different M^{z+} is to be made with a view to delineate the interactive preferences of different M^{z+}.

The relationship between the stability constants of the M^{z+}–carrier complex and the rates of cation transport has been examined. With respect to the log K values of the M^{z+}–carrier complex in methanol and transport across the chloroform layer, Lamb et al. concluded [352] that facilitated transport takes place if the log K value for the migrating species is optimum. The optimum log K range for K^+ and Rb^+ is 5.5–6.0 and for Sr^{2+} and Ba^{2+} is 6.5–7.0; no transport is noted for any M^{z+} for log K below 3.5–4.0. Obviously, the optimum range of log K is quite narrow, beyond which transport efficiency is markedly reduced.

As noticed with homogeneous phase studies and extraction, transport phenomena have also been studied primarily with M^+ rather than with M^{2+}. Transport of M^{z+} may not be possible with every crown. Thus, 12C4 is ineffective towards M^+ as well as M^{2+} [353] perhaps because it is too small to provide an electron-rich interior for the cation, and to provide an adequate hydrophobic exterior to the non-polar solvent. For this crown, $H^{+\delta}$

complexation and crown hydration will also greatly affect the efficiency. 18C6 [353] and 21C7 [353] selectively transport the best-fit K^+ and Cs^+ respectively across a water–chloroform–water system. Selectivity (in complexation as well as transport) attributable to cation–cavity size compatibility does not appear to apply to crowns larger than 21C7, for they are larger than the largest M^{z+} [245,353]. However, for a given crown the selectively complexed cation may not be selectively transported. The following observations are illustrative.

(i) For 18C6, the selectively complexed cation among M^{2+} is Ba^{2+} while the selectively transported cation across a chloroform layer is Sr^{2+} [353]; the Ba^{2+}–18C6 complex is too stable (log $K = 7.04 \pm 0.08$) [245].

(ii) Although the cation selectively complexed by 15C5 is K^+ [245], the one selectively transported across a chloroform layer is the best-fit Na^+ [353]. The unfavourable transport of K^+ has been explained [353] in terms of the reduced availability of the crown which has been used for sandwich encapsulation.

(iii) The order of transport of M^+ and M^{2+} by DC18C6 across a water–toluene–water emulsion membrane is $Cs^+ > Rb^+ > K^+ \geqslant Na^+$ and $Ca^{2+} > Sr^{2+} > Ba^{2+}$ [364] (Li^+ and Mg^{2+} not studied); the best-fit K^+ and Ba^{2+} are poorly transported perhaps because of a different physical environment involved during transport.

As expected, substitution of aromatic or alicyclic nuclei modifies the transport efficiency of the crowns but the modification patterns may be unpredictable. In general, benzo-substituted crowns result in lower transport rates than the cyclohexano or non-substituted crowns [353]; the fall in the

TABLE 3.

The cation-dependent difference in the transport efficiency of 18C6-cavity crowns (from ref. 353)

Cation	Log (moles transported $\times 10^7$ per 24 h)			
	18C6	B18C6	DB18C6	DC18C6
Li^+	[a]	[a]	[a]	0.00 ± 0.10
Na^+	1.05 ± 0.02	0.76 ± 0.10	0.62 ± 0.01	1.36 ± 0.06
K^+	2.44 ± 0.05	2.33 ± 0.05	2.00 ± 0.01	2.53 ± 0.09
Rb^+	2.33 ± 0.08	1.95 ± 0.10	1.08 ± 0.15	2.37 ± 0.06
Cs^+	1.89 ± 0.03	1.04 ± 0.08	0.30 ± 0.20	1.92 ± 0.01
Mg^{2+}	[a]	[a]	[a]	[a]
Ca^{2+}	1.42 ± 0.02	0.52 ± 0.17	[a]	2.21 ± 0.01
Sr^{2+}	2.50 ± 0.03	2.06 ± 0.07	[a]	2.65 ± 0.06
Ba^{2+}	1.26 ± 0.13	0.00 ± 0.20	0.20 ± 0.08	2.45 ± 0.06

[a] The rate of cation transport is less than 0.3×10^{-7} mol transported per 24 h.

transport rate because of benzo group(s) is more pronounced for M^{2+} than for M^{+}. The following are specific observations.

(i) For the 18C6–cavity crowns, the transport efficiency towards a given cation is in the order DC18C6 > 18C6 > B18C6 > DB18C6 (Table 3) [353]. Although the difference between the transport rates for DC18C6 and 18C6 is not much in most cases, the higher rates for DC18C6 can be understood in view of its reduced water solubility so that the carrier loss to the aqueous phase is less [353]. However, this argument is not applicable to, say DB18C6 which is even more insoluble in water [10]. For B18C6 and DB18C6, the advantage provided by the insolubility factor appears outweighed by their relatively weak complexing ability. Substitution on the crown ring may also modify the transport sequences. Whereas the transport sequence for M^{+} with 18C6, B18C6 or DC18C6 is $K^{+} > Rb^{+} > Cs^{+} > Na^{+}$, that with DB18C6 is $K^{+} > Rb^{+} > Na^{+} > Cs^{+}$ [353]. Also, the best-fit K^{+} does not experience a greater change in the transport rate although Rb^{+} and Cs^{+} are, in particular, distinctly affected.

(ii) Again, the transport rate shown by DC30C10 for M^{+} and M^{2+} (excluding Li^{+} and Mg^{2+}) is higher than that for DB30C10 [353]. However, the difference in their transport rates (except for Cs^{+}) is far greater than that between DC18C6 and DB18C6. This is perhaps because no cation matches well the cavities of these crowns and the substitution effects are pronounced.

As discussed with respect to the homogeneous phase and extraction studies, transport of an M^{z+} by a crown is influenced by the nature

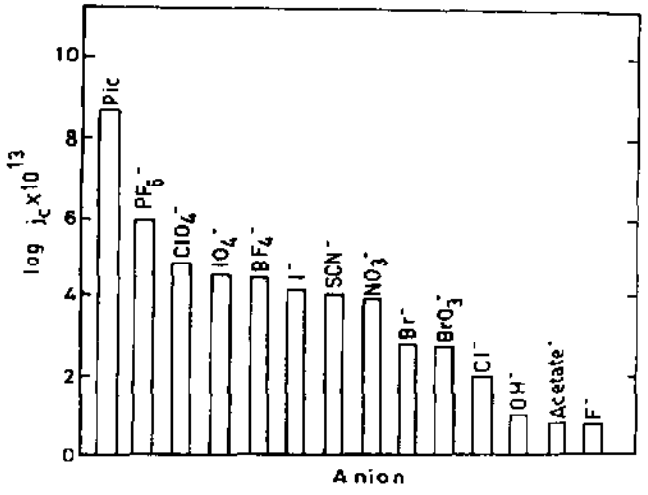


Fig. 22. The effect of the counter-anion on the transport efficiency of K^{+} across a chloroform liquid membrane.

TABLE 4

Variation in transport rate of Sr^{2+} in various Sr^{2+}–M^{z+} mixtures: representative results from ref. 365

Crown	Flux values (in terms of 10^{-3} mol (s m^2)$^{-1}$							
	$\frac{Sr^{2+}}{Li^+}$	$\frac{Sr^{2+}}{Na^+}$	$\frac{Sr^{2+}}{K^+}$	$\frac{Sr^{2+}}{Rb^+}$	$\frac{Sr^{2+}}{Cs^+}$	$\frac{Sr^{2+}}{Mg^{2+}}$	$\frac{Sr^{2+}}{Ca^{2+}}$	$\frac{Sr^{2+}}{Ba^{2+}}$
18C6	$\frac{465}{0.5}$	$\frac{414}{4.4}$	$\frac{256}{87}$	$\frac{456}{41}$	$\frac{612}{58}$	$\frac{700}{0.18}$	$\frac{695}{1.6}$	$\frac{60}{32}$
21C7	$\frac{78}{0.9}$	$\frac{76}{2.8}$	$\frac{53}{53}$	$\frac{55}{143}$	$\frac{53}{180}$	$\frac{117}{0.2}$	$\frac{83}{0.9}$	$\frac{3.5}{71}$

(nucleophilicity or solvation energy) of the counter-anion [345,347,351,362, 367]. Lamb et al. [351] made a detailed study of this point through transport studies on M^{z+} across a water–chloroform–water system. The general conclusions were (i) that transport is favoured as a "small" anion such as Cl^- or OH^- is replaced by a "large" one such as pic^-, $H_2PO_4^-$ or NO_3^- and as a multiply charged anion such as HPO_4^{2-} is replaced by a monovalent analogue, $H_2PO_4^-$ (Fig. 22), and (ii) that a reverse relationship exists between transport of an M^{z+} (in moles per hour) and Gibbs energy of hydration for the counter-anion. Here it is likely, however, that in addition to its hydration features, the anion may influence cation transport through electrostatic (and coordinative) involvement with the cation. This is so because (i) the cation–anion involvement is determined by the same property of the anion (basicity or nucleophilicity) which also determines anion solvation, (ii) transport of a cation with a carrier in such systems is related to the equilibrium constant of the cation–carrier complex (say in methanol), and (iii) the counter-anion determines the equilibrium constant of the cation–carrier complex.

Christensen et al. [366] employed six anions (pyrophosphate, thiosulphate, hydroxide, chloride, formate and nitrate) for a water–toluene–water emulsion membrane and found that an anion can exercise influence on M^{z+} transport even if it is present in the receiving phase. However, if M^{z+} transport is to occur, the stability of the M^{z+}–crown complex has to be less than that of the M^{z+}–anion species.

Ion-transport studies containing binary mixtures of cations in the source phase have been made [350,354,364,365,368]. The transport rate of the common cation in a series of mixtures does not remain constant for a given crown but varies with the other cation involved in the binary mixture. This is understandable in view of the different degrees of competition offered by the different cations (Table 4). The best-transported cation may not signifi-

cantly inhibit the transport of the other cation present in the binary mixture; for the Sr^{2+}–Cs^+ mixture, the transport rate of the best-fit Cs^+ with 21C7 is no doubt higher but that of Sr^{2+}, too, is considerable [365]. Also, the best-transported cations among M^+ and M^{2+} by 18C6 are both K^+ and Sr^{2+} but for the Sr^{2+}–K^+ mixture Sr^{2+} is transported more than K^+ [365].

Interest in "uphill" (active) transport [346,371] is noted even for the electrically neutral crowns. The energy needed for effecting active transport against the concentration gradient is met through an opposite proton flow. Using DB18C6 as a carrier in a liquid membrane, containing a chloride-solvating agent (*m*-cresol) and a diluent (*p*-nonylphenol), active transport of K^+ [371] from a solution containing a mixture of KCl and $MgCl_2$ can take place. The membrane is practically impermeable to Mg^{2+} while it is substantially permeable to water and K^+. The energy for this type of transport is provided by the dilution of the co-solute salt with water that is transferred in the opposite direction. There is also interest in the study of anion transport which is a result of the fact that the transporting cation also drags its counter-anion. This has led to the transport study of organic anions such as pic^- [349] and the amino-acid anions [357,359,369,370]. The correct choice of the counter-cation is naturally of importance. For DB18C6 as the carrier, for example, K^+ has been found to be more suitable than Na^+ in promoting amino-acid anion transport [357] which is understandable for this crown.

(ix) Theoretical studies

In view of the many approximations required to arrive at useful conclusions, theoretical studies of M^{z+}–crown complexes have not been widespread. Work continues to be restricted because of the large number of atoms involved in the crowns although the high symmetry has considerably eased the situation.

Pullman et al. [78] reported the first theoretical study, an ab initio model study on the Li^+–12C4 system. They did not incorporate solvation energy terms and the approach was of rather limited scope. Out of the two possible conformations of 12C4, viz. the maxidentate and the alternate, the former was studied for binding with the cation and it was concluded that complexation with the most stable staggered maxidentate is rather unfavourable; complexation accompanies modification of conformation, of course.

Yamabe and coworkers [79,82] made more detailed theoretical studies on the nature of the interaction between crowns (12C4 and 18C6) and M^+, where $M^+ = Li^+$ [82], Na^+ [79,82] and K^+ [79,82]. For evaluation of the complexation energy, participation of the *p*-orbitals of M^+ ($M^+ = Na^+$ or K^+), through which charge transfer takes place, was considered [79] essential. The CNDO/2 study also revealed that the contribution of the covalent interaction owing to charge transfer is dominant. Through a later ab initio

study [82], they defined the scope of the statement by suggesting that in complex formation electrostatic interaction between the lone pair orbitals of the crown oxygens and the cation does not play a dominant role in the stabilization energy.

Through a molecular mechanics study of the M^+–18C6 complexes (M^+ = Na^+, K^+, Rb^+ and Cs^+), Wipff et al. suggested [80] that different structures adopted in various M^+–crown complexes are a result of the intrinsic property of the individual structures rather than the result of a crystal packing effect. However, it appears that the influence exercised through the coordinative characteristics of M^{z+} is operative. In addition, it has been realized [80] that the structures proposed through optimization steps during theoretical calculations may not be as superior as the X-ray structural results.

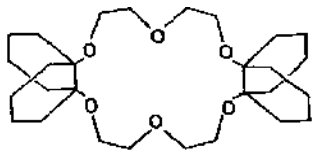
Theoretical studies infer [79] that the role of solvation is more important than the ion–cavity concept towards complexation. Under certain conditions the cavity concept may not even be valid and evaluation of complexation stability using the cavity concept for theoretical calculations has even been cautioned [82]. CNDO/2 studies [79] revealed that the Na^+–18C6 complex is more stable than the K^+–18C6 complex—a result which has been supported through a subsequent molecular mechanics study [80] and through experimental observations [211].

C. CROWN-RELATED MACROCYCLES

Macrocycles of this class are related to Pedersen's original crowns but may carry (a) a special substituent on the ring such as a decalin nucleus or a chiral moiety, (b) a neutral side chain containing oxygen or nitrogen atom(s), (c) a ring containing one or more (or even all) non-oxygen donor atoms, (d) a ring substituent of the amide and diester type, or (e) acidic group(s) or a moiety containing an unpaired electron. A macrocycle of this class may also be a multicavity crown or one with cavity immobilized on a polymer network. We now discuss them in sequence.

(i) Category 1: simple crown-related macrocycles

Replacement of one or both cyclohexano nuclei of DC18C6 by decalin moieties (e.g. **I**, Fig. 23) leads to a macrocycle with improved complexing ability towards Na^+ and K^+ [394]. The substituent effect appears to be partly electronic and partly arising from the modification of the molecular flexibility. In **II**, the di-1-naphthylmethyl units serve the purpose of fixing their strand in such a way that conformational changes become slow enough to enable monitoring of M^{z+} complexation by ^1H or ^{13}C NMR [395]. A



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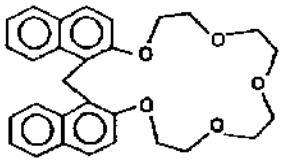

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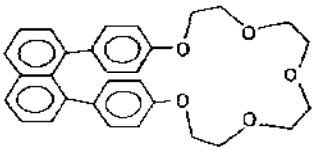
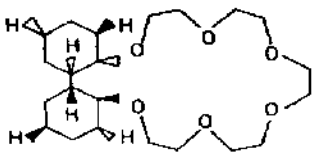


III



IV

Fig. 23. Category 1 crown-related macrocycles (simple crown-related macrocycles): I–IV.

macrocycle containing the anthracene nuclei [396] has been found to be interesting from the viewpoint of obtaining a photochromic crown.

Macrocycle **III** is distinguishable in the sense that although like 15C5 or B15C5 it carries a ring with five oxygens, its complex with KNCS [397] is 2 : 2 dimeric (X-ray analysis) instead of a 1 : 2 sandwich. One of the two oxygens joined to the aromatic moiety is non-interacting (K^+–O, 3.254 Å) while the other forms the longest bond (Table 5); K^+ appears to force a 2 : 2 dimerization (Fig. 24) because of inadequate coordinative saturation provided by the macrocycle as noted for $(KNCS)_2$(DB24C8) [177,178].

Chiral macrocycles have been extensively investigated mainly by Cram and coworkers [398,399], Stoddart [400] and Merz et al. [401]. They possess modified complexing ability towards M^{z+}. For **IV** in $CDCl_3$, for example, the association constants are in the sequence $K^+ > Rb^+ \gg Na^+ > Cs^+ \sim Li^+$ [402] for pic^- as the counter-anion.

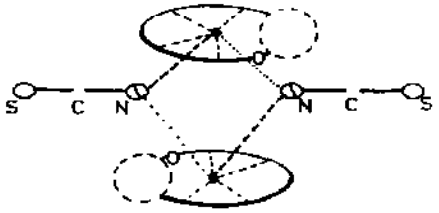


Fig. 24. A schematic view of 2 : 2 KNCS–**III** complex, viz. $[KNCS(III)]_2$.

TABLE 5

Crystallographic description of solid M^{z+} complexes of crown-related macrocycles

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
[KNCS(III)]$_2$ [a]	K^+–O 2.80–2.92 K^+–N 2.91 K^+–N(bridge) 2.93	6 (hexagonal)	397
NaNCS(XII)	Na^+–O av. 2.43 Na^+–N 2.33	6	416
K_3(XII A)$_2Br_3 \cdot 7H_2O$ [b]	K^+–O 2.73–2.84 K^+–O(carbonyl) 2.77	7	417
[K(XIII)$_2$]NCS [c]	K^+(1)–O 2.82–2.99 K^+(2)–O 2.76–3.09	10	419
NaBr(XIV) [d]	Na^+–O 2.37–2.45 Na^+–Br^- 2.76	6	420
Sr(ClO$_4$)$_2$(XV) [e]	Sr^{2+}(1)–O 2.62–2.78 Sr^{2+}(1)–O(ClO_4^-) 2.55, 2.69 Sr^{2+}(2)–O 2.61–2.75 Sr^{2+}(2)–O(ClO_4^-) 2.63, 2.72	8	421
[RbNCS(XIX)]$_2$	Rb^+–O 2.95–3.08 Rb^+–O(NO_2) 3.09, 3.81 Rb^+–N not mentioned	7 (irregular hexagonal pyramid)	424
[CsNCS(XIX)]$_2$ [f]	Cs^+–O 3.04–3.25 Cs^+–O(NO_2) 3.30, 3.57	7	425
[Li_2(XLIX)(H_2O)$_2$](I_2,2H_2O) [g]	Li^+–O 1.98–2.21 Li^+–OH_2 1.93, 1.96	5 (distorted trigonal bipyramid)	456
[K(LI)]$_2$(NCS)$_2$ [h]	K^+–O 2.75–3.06	10	458
[Ba(LI)]$_2$(NCS)$_4 \cdot 4H_2O$ [i]	Ba^{2+}–O 2.75–3.02	10	458
[K(LII)]Cl$\cdot n H_2O$	K^+–O 2.68–2.74	8 (approx end-capped trigonal prism)	461
$KClO_4$(LIII)	K^+–O 2.67–2.85 K^+–O(ClO_4^-) 2.92	8 (end-capped trigonal prism)	464
Rb(pic)(LIV)$\cdot 0.75H_2O$			462
A: [Rb(LIV)]pic	Rb^+–O 2.95–3.37	9	
B: [Rb(pic)(LIV)]$_2 \cdot H_2O$	Rb^+–O 2.92–3.28 Rb^+–O(*p*-NO_2) 2.93 Rb^+–OH_2 3.08	11	
[Mg(LV)(H_2O)](ClO$_4$)$_2$	Mg^{2+}(1)–O 2.42–2.49 Mg^{2+}(1)–OH_2 2.06	8	465
	Mg^{2+}(2)–O 2.12–2.58 Mg^{2+}(2)–OH_2 2.05	8	
[K(LVII)]NCS [j]	K^+–O 2.82–2.84 K^+–N av. 2.86	7 (hexagonal pyramid)	472

TABLE 5 (continued)

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
[Na(LX)]NCS·MeOH	Na^+–O 2.41–2.48 Na^+–N 2.68, 2.70	6	475
$NaClO_4$(LXI)	Na^+–O 2.33–2.49 Na^+–N 2.66 Na^+–O(ClO_4^-) 2.39 Na^+–Cl^- (bridge ClO_4) 2.66	7	476
[Na(LXVII)]I	Na^+–O 2.43–2.61 Na^+–N 2.63, 2.64	8	494
KI(LXVI)	K^+–O 2.79–2.91 K^+–N 2.95 K^+–I^- 3.43	7	494
[Rb(LXXV)(H_2O)]I	Rb^+–O 2.83–2.94 Rb^+–N 3.16, 3.24 Rb^+–N(bridge) 3.34, 3.36 Rb^+–OH_2 3.15	9	495
[Li_2(LXXVI)(H_2O)]Cl_2 ·H_2O	Li^+(1)–N 2.08–2.35 Li^+(1)–O 1.95 Li^+(2)–O 1.92–1.94 Li^+(2)–OH_2 1.93	5 4	497
[Na(LXXVI)]NCS	Na^+–N 2.58–2.64 Na^+–O 2.39–2.53	7	498
[K(LXXVI)]NCS	K^+–N 2.83–2.91 K^+–O 2.66–2.87	8	498
NaNCS(LXXVIII)	Na^+–O 2.48–2.58 Na^+–N 2.40	6	503
[K(LXXVIII)]NCS [k]	K^+–O 2.77–2.87 K^+–S 3.28	6	504
[RbNCS(LXXVIII)]$_2^1$	Rb^+–O 2.86–3.04 Rb^+–S 3.37 Rb^+–N(NCS^-) 3.17 Rb^+–S(NCS^-) 3.43 Rb^+–S(bridge) 3.47		505
[Ba(LXXXI)$_2$](BPh_4)$_2$	Ba^{2+}–O 2.91–3.02 Ba^{2+}–N 2.96–3.08	12 (dodecahedron)	516
[Ba(LXXXII)$_2$(H_2O)$_2$] [Co(NCS)$_4$]	Ba^{2+}–O av. 2.86 Ba^{2+}–N 3.02–3.11 Ba^{2+}–OH_2 2.77, 3.00	11	517
Sr(NCS)$_2$(LXXXIII)·H_2O	Sr^{2+}–O,N 2.69–2.80 Sr^{2+}–OH_2 2.58 Sr^{2+}–N(NCS^-) av. 2.63	9	518
[Mg(LXXXV)(H_2O)$_2$]Cl_2 ·4H_2O	Mg^{2+}–N 2.24–2.31 Mg^{2+}–OH_2 av. 2.10	7 (pentagonal bipyramid)	519

TABLE 5 (continued)

Compound	Bonding features of the cation		Ref.
	Bond distance (Å)	Coordination number (stereochemistry)	
$Ca(NCS)_2$(LXXXVI)	Ca^{2+}–O,N av. 2.64 Ca^{2+}–N(NCS^-) not mentioned	8 (hexagonal bipyramidal)	525
$Sr(NCS)_2$(LXXXVI)·H_2O	Sr^{2+}–O,N av. 2.78 Sr^{2+}–OH_2 2.59 Sr^{2+}–N(NCS^-) not mentioned	9	525
$Ba(NCS)_2$(LXXXVII)·H_2O	Ba^{2+}–O 2.81–2.87 Ba^{2+}–N 3.03 Ba^{2+}–S 3.23, 3.29 Ba^{2+}–OH_2 2.76 Ba^{2+}–N(NCS^-) av. 2.80	9	526
$Ba(ClO_4)_2$(LXXXVIII)	Ba^{2+}–N 2.84–2.89 Ba^{2+}–O(ClO_4^-) 2.92–3.06	10	523
[$SrCl_2$(LXXXIX)]·$2H_2O$	Sr^{2+}–N 2.71–2.74 Sr^{2+}–Cl^- 2.92, 2.93	8 (hexagonal bipyramid)	521
KNCS(XCI)	K^+–O av. 2.75 K^+–N 2.87, 294	8	550
KNCS(XCIII)	K^+–O av. 2.78 K^+–N 2.83 K^+–N(NCS^-) 2.92 K^+–S(NCS^-) 3.40	8	551
KNCS(CIII)	K^+–O 2.77–3.07 K^+–N 2.80	8	552
KNCS(CIV)			553
A: [KNCS(CIV)]$_2$	K^+–O 2.76–3.09 K^+–O(CO) 3.05 K^+–O(CO; bridge) 2.85 K^+–N 2.74	8 (distorted bipyramid)	
B: [KNCS(CIV)]	K^+–O 2.69–3.21 K^+–O(CO) 2.59 K^+–N 2.71	7	
$Mo(CO)_3$(PhCOLi)[$(Ph_2POCH_2CH_2)_2NCH_2CH_2OCH_3$]	Li^+–O 1.92–2.09 Li^+–N 2.23	5 (trigonal bipyramid)	510
[Li(CXXVII)]$FeCl_4$[m]	Li^+–O 2.00–2.09	5	628
[Li(CXXVIII)]Cl [n]	Li^+–O 2.03–2.42	7	628
[Na(CXXXVII)]BF_4	Na^+–O 2.47–2.50 Na^+–N 2.64–2.65	8 (cubic)	654

TABLE 5 (continued)

[a] Of the two oxygen atoms attached to the aromatic moiety, one is "non-interacting".
[b] The structure consists of hydrated polymeric chains formed by the repetition of the dimeric unit $[\{K(\mathbf{XII}\ A)\}_2 3H_2O]^{2+}[KBr_3,4H_2O]^{2-}$.
[c] Thiocyanate is charge separated from K^+ and is hydrogen bonded to the pendant OH function of **XIII**.
[d] The *o*-dimethoxy groups of **XIV** are "non-interacting" towards the cation.
[e] The acetyl group of **XV** is "non-interacting" towards the cation.
[f] The longer $Cs^+-O(NO_2)$ bond is rather too long for a contact and NCS^- is disordered.
[g] Two oxygen atoms of each hexaether moiety of **XLIX** are hydrogen bonded to a water molecule while an oxygen lies "idle"; Li^+ is charge separated from I^- which is hydrogen bonded to a cation-coordinated water molecule.
[h] Potassium charge separated from NCS^-; dimerization occurs because of the interaction of the cation with two pentaether moieties of two separate molecules of **LI** and not because of NCS^- which is disordered.
[i] Thiocyanate and water molecules form infinite hydrogen-bonded chains.
[j] There is a very weak interaction between K^+ and NCS^- (3.33 Å).
[k] There is a weak interaction between K^+ and NCS^- (3.04 Å).
[l] Thiocyanate crystallographically disordered but chemically interacting.
[m] There is an additional long contact at 2.88 Å.
[n] There is an additional long contact at 3.48 Å.

(ii) Category 2: macrocycles carrying electrically neutral substitutions on the crown ring

A number of macrocycles containing electrically neutral substituents on the crown ring have been synthesized and their binding ability towards M^{z+} has been evaluated [210,403–416]. The most conspicuous among them are the "lariat ethers" (e.g. **V**, Fig. 25) synthesized by Gokel and coworkers [403–407]. The cognomen "lariat" stands for a conceptual similarity between these molecules and the lassoes which are used to rope and tie animals; the donor ring ropes the cation while the side-arm donor group further ties it up. Herein, work with C-pivot lariat ethers is described while N-pivot lariat ethers are treated under category 5. In 90 vol.% MeOH–10 vol.% H_2O [404] these macrocycles have shown a general decreased binding ability compared with the parent crowns which is not in tune with their enhanced extracting ability reported earlier [403]. The decreased and solvent-dependent binding ability of these macrocycles is perhaps because of a heavy hydrogen-bonding (solvation) of the side-arm which may partially block the crown hole. Nevertheless, a number of lariat ethers have shown a modestly enhanced binding ability towards Na^+ and K^+ [407] which is understandable because of the geometric arrangement of the side-arm which provides additional interacting sites. A quaternary methyl group bonded to

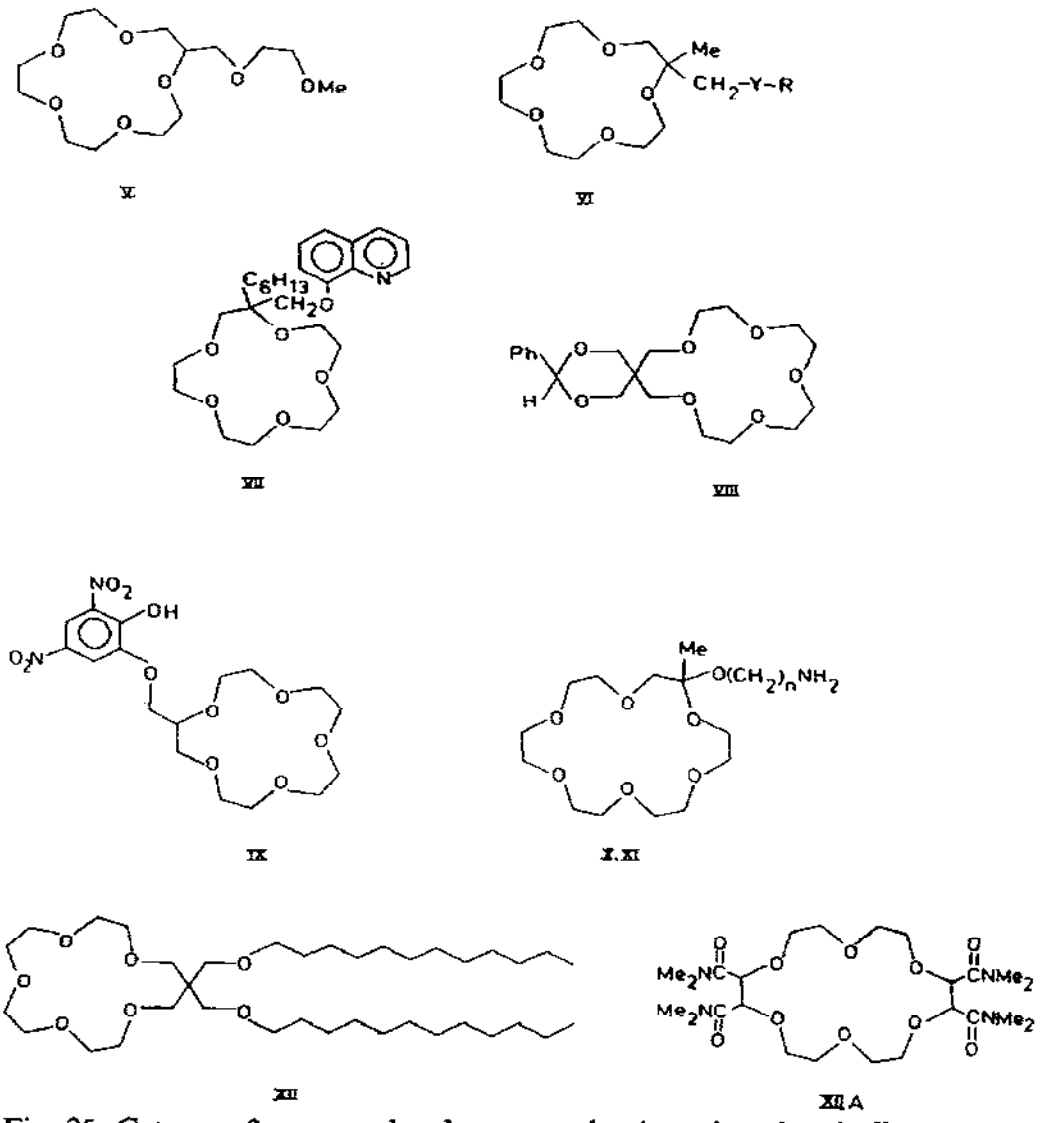


Fig. 25. Category 2 crown-related macrocycles (carrying electrically neutral substituents on the crown ring): **V–XII A** (for **VI**, Y can be O, S or NH and R can be a long group; **X**, $n = 5$; **XI**, $n = 2$).

the pivot carbon alters the binding ability of, for example, **VI** [405] (Table 6).

Nakatsuji et al. have demonstrated a distinct role played by the side-arm with respect to the Na^+/K^+ selectivity [408]. Whereas 15C5 shows practically no selectivity for any M^+, the Na^+/K^+ selectivity of **VII** is 27.5. This could be because the side-arm contains the N-donor 8-hydroxyquinoline moiety. The macrocycle **VIII**, spiro-16-crown-5, is also Na^+ selective [412]. Macrocycles containing chromogenic units (dye units) have also been

TABLE 6

Cation-dependent modifications in lariat ether binding abilities induced by a quaternary methyl group (from ref. 405)

Compound	Substituents in the 2-positions of 15-crown-5	Log K_s in MeOH at 25 °C	
		Na^+	K^+
15C5	H, H	3.27 [a]	3.60 [a]
		3.31 [b]	3.34 [b]
		3.48 [c]	3.77 [c]
VIa	H, $CH_2OCH_2CH_2OCH_3$	3.05	3.32
VIb	CH_3, $CH_2OCH_2CH_2OCH_3$	3.87	3.42
VIc	H, $CH_2O(CH_2CH_2O)_2CH_3$	3.13	3.50
VId	CH_3, $CH_2O(CH_2CH_2O)_2CH_3$	3.89	3.98
VIe	H, $CH_2O(CH_2CH_2O)_3CH_3$	3.09	3.50
VIf	CH_3, $CH_2O(CH_2CH_2O)_3CH_3$	3.87	4.00

[a] Values determined at the University of Maryland (the Gokel group).
[b] Values determined at Osaka University (the Okahara group).
[c] J.D. Lamb, cited in ref. 52.

synthesized [413] and used for spectrophotometric determination of Na^+ and K^+; macrocycle **IX** for the spectrophotometric determination of Na^+ in human serum, for example.

The macrocycles **X** and **XI**, however, can effect a selective and active transport of K^+ over Na^+ across a liquid membrane [411]. In actual practice, the macrocycle is made to complex K^+ in a basic source phase which is transported to an acidic receiving phase. K^+ is released in the acidic phase and the amino group of the side-arm of the macrocycle gets protonated. The primary ammonium ion thus formed undergoes in situ intramolecular complexation with the macrocycle ring. When this species returns to the interface of the membrane and the so-called "source phase", H^+ is released and a K^+ ion is again taken up to complete the cycle.

The macrocycle **XII**, for example, contains two dodecyloxymethyl side-arms joined on a single carbon atom but in NaNCS(**XII**), for example, (Fig. 26) the oxygen atoms of the side-arms do not coordinate with the cation

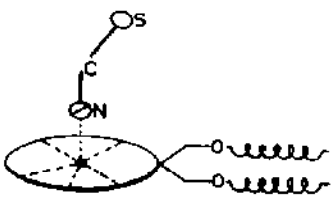


Fig. 26. A schematic view of NaNCS(**XII**).

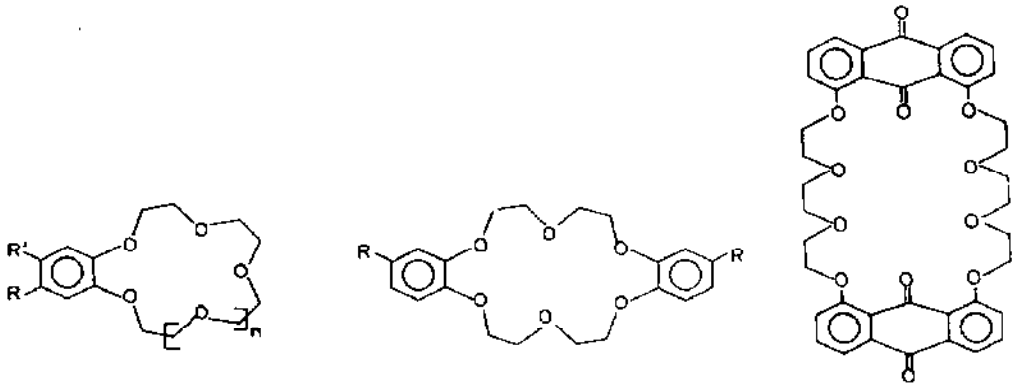


Fig. 27. Category 3 crown-related macrocycles (carrying substituted aromatic nucleus) **XIII–XXVII: XIII**, R = H, R′ = OH, $n = 1$; **XIV**, R = R′ = OMe, $n = 1$; **XV**, R = H, R′ = COMe, $n = 2$; **XVI**, R = H, R′ = COMe, $n = 1$; **XVII**, R = H, R′ = $-CH(OH)-CH_2-N(H)(CH_3)$, $n = 2$; **XVIII**, R = H, R′ = $-CH(OH)-CH_2-N(H)(CH_3)$, $n = 1$; **XIX**, R = H, R′ = NO_2, $n = 2$; **XX**, R = H, R′ = NO_2, $n = 1$; **XXI**, R = H, R′ = NH_2, $n = 1$; **XXII**, R = NO_2; **XXIII**, R = NH_2; **XXIV**, R = COMe; **XXV**, R = H, R′ = CH_2OH, $n = 1$; **XXVI**, R = H, R′ = CH_2OMe, $n = 1$.

[416] (X-ray analysis). True to its own Lewis acidity, Na^+ forms an ion-paired complex also interacting with NCS^- (Table 5). The 3 : 2 complex of KBr with **XII A**, wherein the side-arm coordinates with K^+, has been proposed by Lehn's group [417] as a solid state model of a transmembrane channel (Table 5).

(iii) Category 3: macrocycles carrying a substituted aromatic nucleus

The benzo-based substituted crowns and similar macrocycles (**XIII–XXVII**, Fig. 27) are being investigated [143,192,304,363,418–429]. The substitution of the four benzo-hydrogens by four fluorines in B15C5 and B18C6 causes a marked decrease in their complexing ability as noted through a poor extraction of Na^+pic^- and K^+pic^- from water to dichloromethane [418]. This observation is comparable to those for tetrabromo- and tetrachloro-DB18C6 wherein 4-[*p*-(dimethylamino)phenylazo] benzene sulphonate has been used as the counter-anion [304]. The halogen atoms obviously exercise a strong −I inductive effect and diminish the basicity of the donor ring. Nevertheless, 4-bromoB15C5 forms a 1 : 2 solid complex with $KClO_4$ [143] indicating its ability to cause ligand encapsulation of the cation.

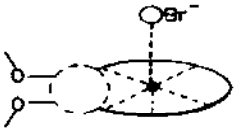


Fig. 28. A schematic view of NaBr(XIV).

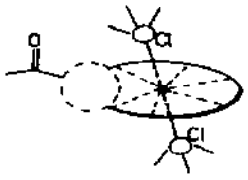


Fig. 29. A schematic view of $Sr(ClO_4)_2$(XV).

With **XIII**, which contains a 4-hydroxyl group at the aromatic nucleus of B15C5 [419], K^+ forms a genuine 1 : 2 charge-separated sandwich as revealed by X-ray analysis (Table 5). The hydroxyl function is, however, not coordinated and is only involved in bonding with NCS^- [419]. The two methoxy groups present in **XIV** [420], do not coordinate (Fig. 28) with the cation in the complex NaBr (**XIV**) (Table 5) obviously because of an unsuitable geometric arrangement of both the pendant groups; Na^+ remains paired with Br^- (Na^+–Br^-, 2.763(3) Å), consistent with the anionphilicity of this cation. The macrocycle **XV**, which carries a 4-acetyl group at the benzo nucleus of B18C6, does not involve the substituent in coordination of the cation as noted through X-ray analysis of $Sr(ClO_4)_2$ (**XV**) [421] (Fig. 29); the rather anionphilic Sr^{2+} prefers pairing with the ClO_4^- anions, one from each axial side, while coordinated by the six ring oxygens.

The role of the counter-anion in the synthesis of the solid M^{z+} complexes of crown-related macrocycles has by and large been neglected, perhaps because the primary aim of such studies has been to monitor the effect of structural changes in the crown ring towards its complexing ability using any suitable cation as a substrate. Nevertheless, results are available. Thus, **XV** shows a rather monotonous 1 : 1 interaction with a variety of MX_z salts ($X^- = NCS^-$ or ClO_4^-), but the lower analogue **XVI** senses a role of the counter-anion and displays an altered M^{z+}–macrocycle stoichiometry; both bivalent Sr^{2+} and Ba^{2+} undergo a 1 : 1 interaction with **XVI** for NCS^- whereas for the much less nucleophilic ClO_4^-, each cation forms a 1 : 2 complex [421].

The adrenaline moiety in **XVII**, present as a substituent on the benzo nucleus of B18C6, has been argued [422] to be non-coordinating towards M^{z+} even though it possesses a secondary amino group and a hydroxyl group. This ligand forms 1 : 1 solid complexes with Na^+ and Mg^{2+} while with Ba^{2+} it forms a rather less reliable 2 : 3 complex. However, the lower analogue **XVIII** shows a 1 : 1 stoichiometry for Na^+ yet 1 : 2 with Ba^{2+} and even Mg^{2+}. It is likely that in the 1 : 2 Mg^{2+} complex one or both MCM exist unchelated.

The complexing behaviour of **XIX** in the solid state contrasts with that shown by **XIII**–**XV** (and expected for **XVI**–**XVIII**) in that the 4-nitro

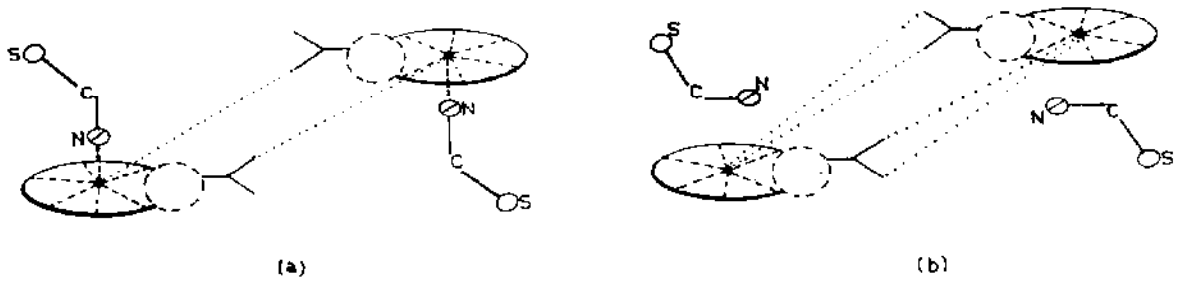


Fig. 30. A schematic view of (a) $[RbNCS(XIX)]_2$ and (b) $[CsNCS(XIX)]_2$.

substituent at the benzo nucleus undergoes coordination with the cation. Uniquely, the macrocycle forms 2 : 2 dimeric complexes with RbNCS [424] and CsNCS [425] (Table 5). The dimerization is caused by interaction of the nitro substituent with the adjoining cation in the lattice so that it acts as a monodentate towards Rb^+ and as a bidentate towards Cs^+ (Fig. 30). The unique dimerizing ability of the nitro group is perhaps a result of the fractional negative charge present on the nitro oxygens in a state directed away from the aromatic nucleus. In these complexes, NCS^- can either be ion paired with the cation (Rb^+) or may exist separated from it (Cs^+).

Incorporation of the 4-nitro group in B15C5 (as in **XX**) drastically decreases [427] the formation constant with Na^+ in acetone (0.365×10^{-3} M^{-1} compared with 3.44×10^{-3} M^{-1} for B15C5), for example. This is obviously because of the electron-withdrawing nature of the substituent. Substitution of a primary amino group at the same position (as in **XXI**), however, causes a dramatic 25-fold increase in the stability value for Na^+ [427] ($K = 8.21 \times 10^{-3}$ M^{-1}) understandably because of its positive contribution towards complexation. The macrocycle **XXII**, which is a dinitro derivative of DB18C6, complexes Na^+ (as NCS^- in DMF) five times less effectively than DB18C6 [492]. However, the corresponding diamino derivative (**XXIII**) displays a complexing power comparable to (instead of being higher than) that of DB18C6. This suggests that the observed substituent effect cannot always be rationalized in a simple manner, the effect also depends on the less-defined chemical environment.

Three-phase facilitated-transport studies across a chloroform membrane for the DB18C6 derivatives reveal that the rate of transport of Na^+ and K^+ is reduced in the order DB18C6 > **XXIV** (containing the acetyl groups) > tetrabromo-DB18C6 > **XXII** > octachloro-DB18C6 [363]. Incorporation of an acetyl group decreases the complexing power. This suggests that in **XV** and **XVI**, the substituent is not idle and exercises an electron-withdrawing effect on the ring. Interaction of Sr^{2+} with both the ClO_4^- anions [421], therefore, can be better rationalized in terms of decreased complexing ability of **XV** compared with that of B18C6.

An effect of the substituents has also been observed in the two-phase extraction studies. Thus, **XXV**, a 4-hydroxymethyl-substituted B15C5, displays decreased extraction efficiency [428] compared with B15C5; for the water–dichloromethane phases, both Na^+ and K^+ are extracted poorly. However, methylation of this group (as in **XXVI**) improves the efficiency over B15C5, because of better electron-releasing properties of the methoxymethyl substituents.

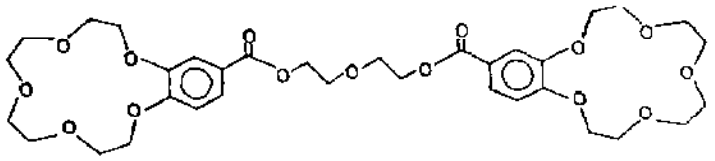
Macrocycles containing an anthraquinone nucleus (or nuclei) (such as **XXVII**) have recently attracted attention [429]. **XXVII** shows the conventional extraction selectivity for M^+ ($K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$) but for M^{2+} it shows a distinct preference for Ba^{2+} over Mg^{2+}, Ca^{2+} and Sr^{2+} (all of which are poorly as well as comparably extracted). Since the ligand in this work has been used in excess it is not certain whether the stoichiometry of the complex remains 1 : 1 for all the cations.

(iv) Category 4: bridged crowns

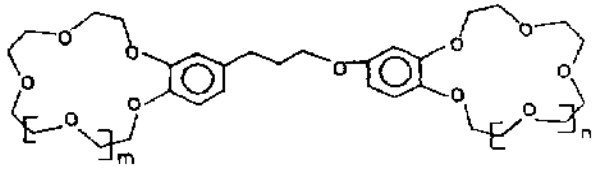
The macrocycles belonging to this category possess more than one crown ring, usually two. These rings may be joined by an intermolecular chain as in **XXVIII**, an intramolecular chain as in **LIV**, or by one or more spiro carbons as in **XLVIII** (Fig. 31). Of the three types, MCM of the first type have been studied most intensively and offer a better design potential for attaining the desired cation selectivity.

Bourgoin et al. introduced [430] for the first time a series of so-called bis-crowns, such as **XXVIII**. Such crowns could be of the following types: symmetrical bis-crowns such as **XXVIII** wherein the component crown moieties as well as the connecting chain are symmetrical; unsymmetric bis-crowns such as **XXIX** wherein the crown moieties are not symmetrical while the connecting chain may or may not be symmetrical; and pseudo-symmetrical bis-crowns such as **XXX** wherein the crown moieties are symmetrical but the connecting chain is not. However, those evaluated for interaction towards M^{z+} have often been of the symmetrical type.

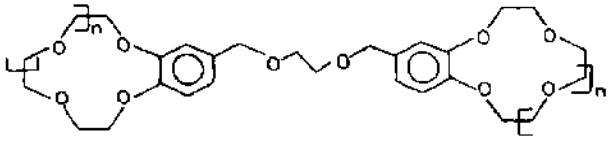
Almost all studies with bis-crowns have involved pic^- salts of M^{z+}. The absorption maximum (λ_{max}) of the anion in the complex is the main criterion for determining the nature of the complex. A pronounced bathochromic shift [430,431] for λ_{max} indicates formation of a loose ion pair complex (i.e. a 1 : 2 cation/crown-unit sandwich complex) while a slight shift indicates tight ion pair formation (i.e. a 1 : 1 cation/crown-unit complex). For example, λ_{max} for K(pic) in THF is at 357 nm but on the addition of **XXVIII**, shifts to 380 nm which indicates 1 : 2 K^+/crown-unit sandwich formation [430]. On the basis of this criterion, the macrocycles **XXXI–XXXIII** [432], carrying B12C4, B15C5 and B18C6 units respectively, exhibit the



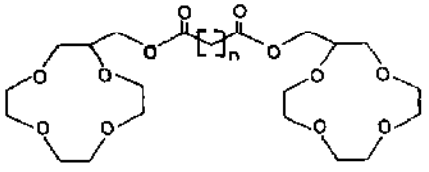
XXVIII



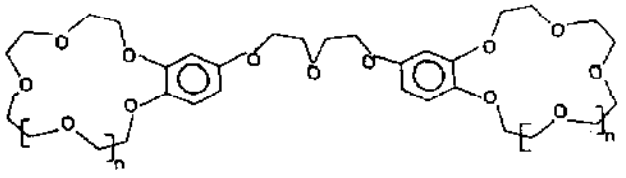
XXIX , XXX



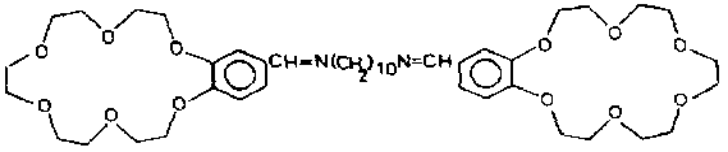
XXXI - XXXIII



XXXIV , XXXV

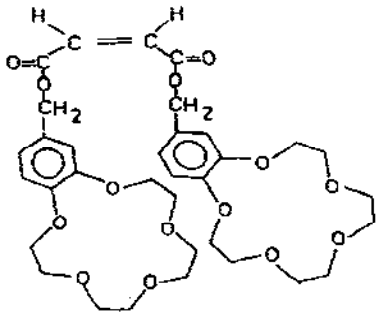


XXXVI , XXXVII

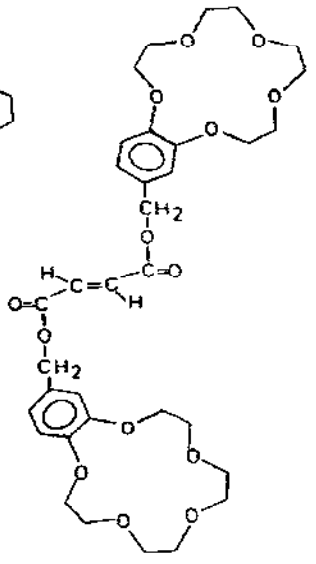


XXXVIII

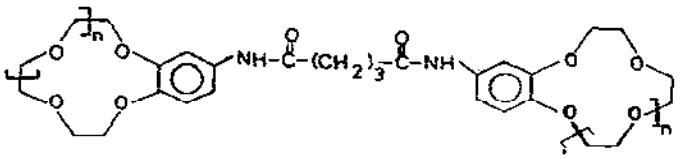
Fig. 31. Category 4 crown-related macrocycles (bridged crowns) **XXVIII–LV**: **XXIX**, $m = 1$, $n = 2$; **XXX**, $m = n = 2$; **XXXI**, $n = 1$; **XXXII**, $n = 2$; **XXXIII**, $n = 3$; **XXXIV**, $n = 1$; **XXXV**, $n = 3$; **XXVI**, $n = 1$; **XXXVII**, $n = 2$; **XLI**, $n = 1$; **XLII**, $n = 2$; **XLIII**, $n = 3$; **XLIV**, X = $C(CH_3)(C_{12}H_{25})$; **XLV**, X = C_2H_4; **XLVIII**, $n = m = 1$; **XLIX**, $n = m = 2$; **L**, $n = 0$, $m = 2$.



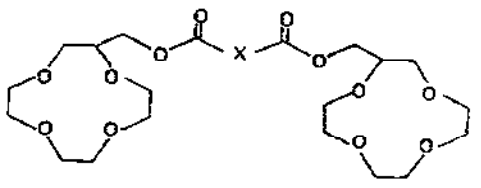
XXXIX



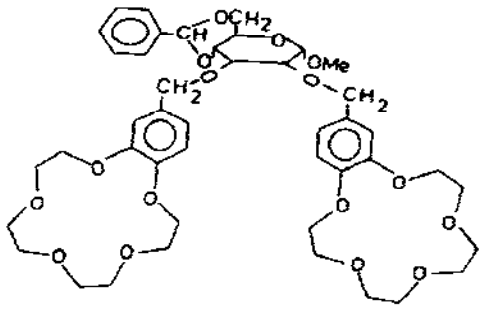
XL



XLI – XLIII

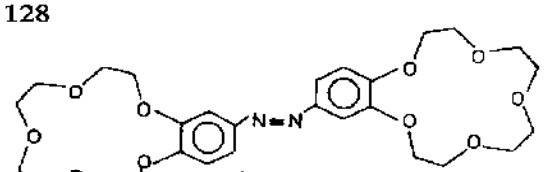


XLIV , XLV



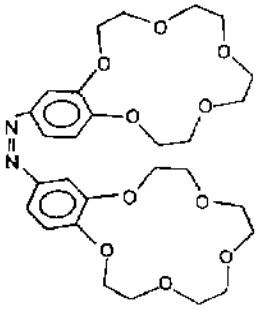
XLVI

Fig. 31. (continued).

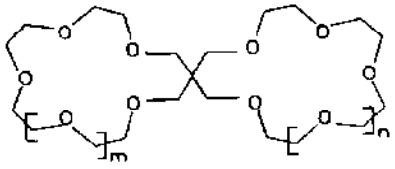


trans - XLVII

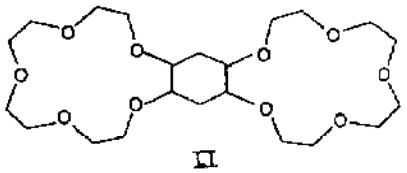
dark ⇅ hν



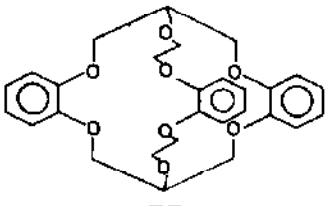
cis - XLVII



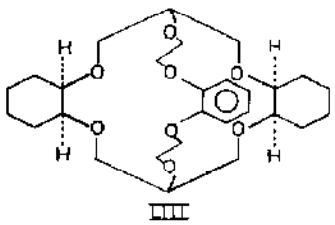
XLVIII - L



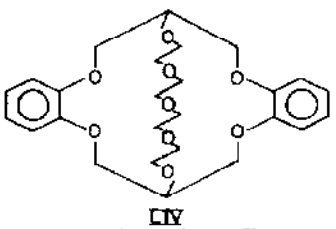
LI



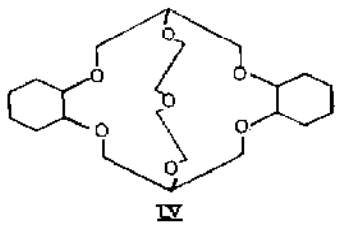
LII



LIII



LIV



LV

Fig. 31. (continued).

following types of complexing behaviour towards some M^+: 1 : 2 sandwich formation, by **XXXI** with Na^+ and K^+, by **XXXII** with K^+, Rb^+ and Cs^+, and by **XXXIII** with Cs^+; 1 : 1 non-sandwich complex formation by **XXXII** with Na^+ and by **XXXIII** with Na^+, K^+ and Rb^+. The 1 : 2 sandwich formation with bis-crowns leads to enhanced extraction, which is understandable because a 1 : 2 complex is, in general, more lipophilic than the corresponding 1 : 1 complex. The extraction sequences for bis-B12C4 crowns (**XXXIV** and **XXXV**), bis-B15C5 crown (**XXXVI**) and bis-B18C6 crown (**XXXVII**) are $Na^+ > K^+ \sim Rb^+ \sim Cs^+$ [433], $K^+ > Rb^+ \gg Cs^+ > Na^+$ [434] and $Cs^+ > K^+ > Rb^+ \gg Na^+$ [434] respectively.

The interaction stoichiometry of Rb^+ towards B18C6-based bis-crowns is intriguing. Thus, λ_{max} of pic^- in the Rb^+–**XXXIII** complex (in chloroform) is 365 nm and the stoichiometry [432] is 1 : 1 while that for Rb^+–**XXXVII** in THF is 371 nm which [434] is a result of a mixture of 1 : 1 and 1 : 2 complexes. These results are intriguing in view of the observations that in dichloromethane, Rb^+–**XXXVIII** absorbs at 374 nm which is "closely approximating" [435] the feature of the loose ion pairs (sandwich complexes); Rb^+–**XXX** in dichloromethane absorbs at 376 nm [436] which implies 1 : 2 sandwich formation.

The structure and length of the chain connecting the two crown moieties are of importance and appear to exercise the following dramatic effects on the complexing behaviour of the bis-crown.

(i) The bis-crown **XXXIX**, derived from maleic acid, forms 1 : 2 sandwich complexes with certain cations (K^+, Rb^+ and Cs^+) [437] whereas **XL**, derived from fumaric acid, cannot form a sandwich with any such cation. This is because of an unfavourable geometry of the connecting chain which prevents cooperation of the crown moieties. Consequently, the extraction efficiency of **XL** towards K^+, for example, is 14 times lower than that of **XXXIX** [437].

(ii) The bis-crowns based on 12C4 or B12C4 units generally undergo 1 : 2 complexation with Na^+ and are Na^+ selective [433,438,439] whereas for **XLI**, which contains a connecting chain possessing two amide groups, the Na^+ selectivity is lost because of 1 : 1 complexation [440]. However, **XLII** and **XLIII** [441], containing the same connecting chain, show behaviour expected for typical bis-15C5 and bis-18C6 crowns respectively.

(iii) **XXXIV**, based on malonyl chloride, shows [433] 1 : 2 sandwich complexation with Na^+ whereas **XXXV**, based on a rather longer chain, shows 1 : 1 complexation with Na^+. Interestingly, with either MCM, extraction of Na^+ is higher than that of K^+, Rb^+ or Cs^+.

(iv) As revealed by potentiometric measurement of the stability constants in methanol, **XLIV**, containing a dodecylmethyl malonate group, is 34 times selective for Na^+ over K^+ [438] whereas **XLV**, containing only a succinate group, is merely 9.5 times selective.

A rigorous examination of the complexing behaviour of bis-crowns reveals some unexpected results.

(i) Except for certain bis-12C4 crowns, Na^+ (as pic^-) undergoes 1 : 1 complexation even in the presence of a large excess of a bis-crown. This is expected in view of size considerations as well as the anionphilic [9] behaviour of this cation. However, in the presence of a 20-fold excess of **XXXVII**, the λ_{max} of pic^- in THF shifts from 352 nm to as much as 381 nm [434] indicating that the bis-crown has imposed sandwich complexation.

(ii) Extraction of Li^+ with any bis-crown is, in general, quite low so that this cation is often excluded from such studies. However, **XLVI** [428], which possesses two B15C5 moieties and a carbohydrate skeleton, surprisingly extracts Li^+ from water into dichloromethane to the extent of 67% (as against 83% for the highest extracted K^+).

Because of the potential displayed by bis-crowns with respect to their selectivity towards M^+, they have been widely used as components of ion-selective electrodes [436,439,442–447]. The Kimura–Shono group reported in 1979 K^+-selective [442] and Cs^+-selective [443] electrodes based on the bis-B15C5 and bis-B18C6 crowns respectively. Fung and Wong [444] reported K^+- and Cs^+-selective electrodes based, respectively, on the bis-B15C5 and bis-B18C6 crowns such as **XXXII** and **XXXIII**, which have the advantage of the hydrolytic stability of the poly(oxyethylene) connecting chain. The Kimura–Shono group introduced coated wire Na^+- and K^+-selective electrodes [439] based on bis-12C4 and bis-B15C5 crowns respectively. Since bis-B15C5 crowns are K^+ selective while bis-B18C6 crowns are Cs^+ selective, an unsymmetrical bis-crown containing a B15C5 moiety (such as **XXIX**) may be expected to be Rb^+ selective. Ikeda et al. [436] indeed devised a membrane selective electrode based on **XXIX** which is Rb^+ selective although $Rb^+/(K^+,Cs^+)$ selectivity is not so high. K^+-selective electrodes with improved lipophilic properties and based on bis-15C5 crowns have recently been reported [446,447].

A new off-shoot in the chemistry of the bis-crowns is the use of photoresponsive bis-crowns so that complexation in general (and extraction and transport in particular) are photoregulated—an aspect which has been studied in fair detail [448–453]. The key principle is that under the effect of light the trans isomer of a bis-crown such as **XLVII** is converted into the cis isomer which is reconverted into the former in the dark. This conversion justifies their trivial name as "butterfly crowns".

By analogy with the relationship of **XXXIX** with **XL**, *cis*-**XLVII** extracts the K^+ salt of methyl orange from water to *o*-dichlorobenzene 42.5 times more effectively than the *trans*-**XLVII** isomer whereas the latter extracts Na^+ 5.6 times more effectively than *cis*-**XLVII** [448]. This, consequently, results in a remarkably large selectivity (238-fold) of *trans*-**XLVII** vs. *cis*-

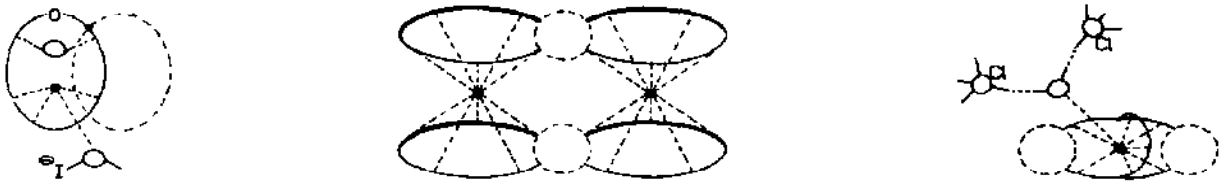


Fig. 32. A schematic view of $[Li_2(\mathbf{XLIX})(H_2O)_2](I_2,2H_2O)$.

Fig. 33. A schematic view of $[M(LI)]_2(NCS)_z$ "double-sandwich" complexes ($M^{z+} = K^+$ or Ba^{2+}); water molecules for the Ba^{2+} complex not shown.

Fig. 34. A schematic view of $Mg(ClO_4)_2(LV)\cdot H_2O$.

XLVII for Na^+ over K^+. For *cis*-**XLVII**, there is a contribution of the sandwiching ability towards K^+ and hence its effective complexation. Strikingly, even in photoinduced ion permeation, an influence of the counter-anion on cation permeation, in accordance with its hydrophobicity, has been noted [451]. Unfortunately, however, studies with the intermolecularly bridged crowns have not been extensive and attention has been focused on M^+ but not on M^{2+}. There is no report on the synthesis of solid M^{z+} complexes or on their structural analysis. Formation constant studies in homogeneous polar media have not been carried out except a few by Bourgoin et al. [430] and Ikeda et al. [438].

In 1979, Weber introduced [454] the so-called multiloop crowns which carry two or more crown moieties joined together by spiro carbon atom(s). He designated such MCM as "spiro crowns". The spiro-bi-crown **XLVIII** containing two 16C5 rings is remarkable in that from an acetone–ethyl acetate solution containing NaNCS and $Ca(NCS)_2$, it exclusively complexes NaNCS even though the cations involved are of comparable size [454,455]. This is in contrast to the exclusive complexation of Ca^{2+} with B15C5 from the NaNCS–$Ca(NCS)_2$ mixture [108] under similar conditions. Also, the 19C6–19C6 analogue, **XLIX**, yields a bimetallic complex with $Ba(NCS)_2$ [455] when added to a 1 : 1 solution of KNCS and $Ba(NCS)_2$ in acetone or when $Ba(NCS)_2$ is added to a 1 : 1 acetonic solution of KNCS and **XLIX**. The unsymmetrical 13C4–19C6 bi-crown, **L**, shows an Li^+/K^+ preference and yields a 1 : 2 solid Li^+–**L** complex. It does not discriminate between Li^+ and Ba^{2+} in that it yields a bimetallic complex containing an ion of each type. Such observations suggest that the charge density (polarizability or polarizing ability) of a cation is linked to its recognition.

Each ring of **XLIX** forms a dihydrated 1 : 1 complex with LiI. X-ray structural analysis [456] of the product reveals that only three of the six oxygens of each ring coordinate with the cation (Fig. 32; Table 5). Of the three remaining crown oxygens in each ring, one is "idle" while the other

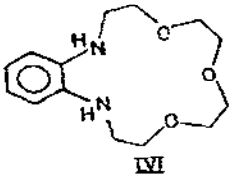
two are blocked through bonding with a double-action water molecule which is also coordinating with the cation. The other water molecule displays double action in that it coordinates with the same cation and also bonds with I^- to keep it separated from Li^+.

^{23}Na NMR studies [457] on the interaction of spiro-crowns with Na^+ in pyridine in the presence of the less nucleophilic ClO_4^- have revealed that both 1 : 1 and 2 : 1 complexes are formed with **XLVIII** as well as **XLIX**. The binding constants of the 2 : 1 complexes, because of electrostatic repulsion between the two bound cations, are lower by an order of magnitude. The series of spiro-crowns has been extended [454,455] to tri- and tetra-crowns but the results are not as exciting as for the bi-crowns.

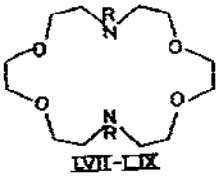
In **LI**, the two 15C5 moieties are connected together by a cyclohexane nucleus [458] which cannot provide the type of flexibility possible through a linear chain. Therefore, **LI** resembles more a spiro-crown than an intermolecularly bridged crown. X-ray structural analysis [458] of the KNCS–**LI** and $Ba(NCS)_2$–**LI** complexes has revealed the complexes to be 2 : 2, constituting a type of "double sandwich" (Fig. 33; Table 5). Each cation, instead of forming an intramolecular sandwich with the two crown moieties, undergoes interaction with two crown moieties of two separate molecules.

Bridged crowns containing an intramolecular chain have also attracted attention [459–465]. **LII**, for example, discriminates Cs^+ from K^+ in that with the former it forms a 1 : 2 solid complex in contrast to a 1 : 1 complex with the latter [460]. In the charge-separated complex, K^+ is coordinated with all eight oxygens of the ligand [461] while the water molecules and the anion are eliminated from the interaction sphere of the cation. However, the related **LIII**, possessing two terminal cyclohexano nuclei instead of the two benzo nuclei, binds only seven out of eight oxygens to K^+ [464] and the rather charge-delocalized ClO_4^- also remains paired with the cation (Table 5). It is surprising that **LIII** displays incomplete coordination even though it possesses the highest complexing power of all its isomers [463].

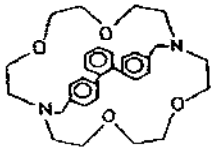
Among M^+, **LIV** is known to complex best with Rb^+ [459]. With Rb(pic), it yields a crystalline 1 : 1 complex containing two crystallographically independent Rb^+ ions [462]. One charge-separated moiety in the complex, Rb(**LIV**)(pic), contains Rb^+ coordinated exclusively with the nine oxygens of the ligand. The other anion-paired moiety, $[Rb(pic)(LIV)]_2 \cdot H_2O$, is unique in composition in that it contains two anion-paired Rb^+ ions which are dimerized by a water molecule. Moreover, the anion in this moiety interacts with the cation, not through the phenolic oxygen, but through an oxygen of the *p*-nitro group; the phenolic site is merely bonded to the second water molecule which is uncoordinated to Rb^+. The Rb^+–phenoxide separation is in accordance with the low charge density of the cation so that an oxygen carrying fractional negative charge gets preference over the



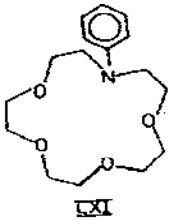
LVI



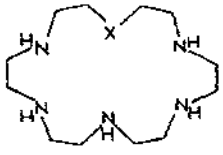
LVII–LIX



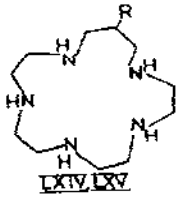
LX



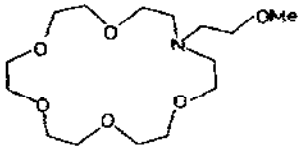
LXI



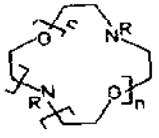
LXII, LXIII



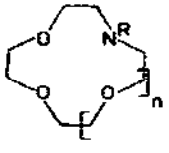
LXIV, LXV



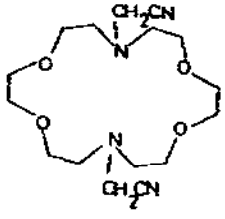
LXVI



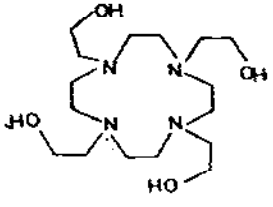
LXVII – LXX



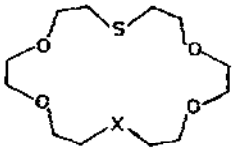
LXXI – LXXIV



LXXV

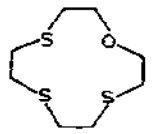


LXXVI

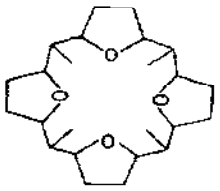


LXXVII, LXXVIII

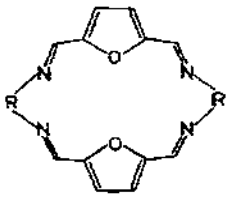
Fig. 35. (See page 135 for the legend.)



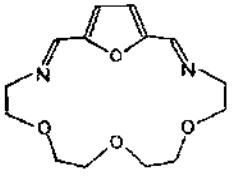
LXXIX



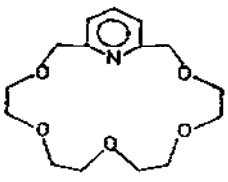
LXXX



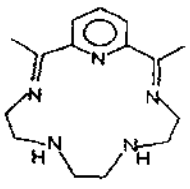
LXXXI , LXXXII



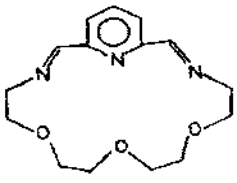
LXXXIII



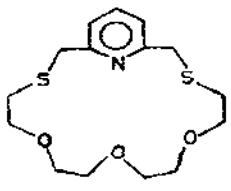
LXXXIV



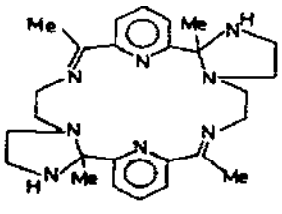
LXXXV



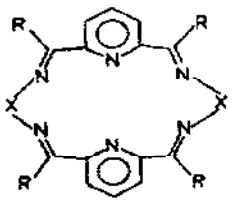
LXXXVI



LXXXVII



LXXXVIII



LXXXIX ,XC

Fig. 35. (continued).

formally charged one. Simultaneous coordination of one water oxygen with two Rb^+ cations is again unique as two water molecules are present but only one water molecule coordinates with two cations. Such a dimerizing role of water is the first example for M^{z+} complexes of crown-related macrocycles. It is also a rare feature for M^{z+} complexes on the whole (see refs. 151, 156 and 186 for other complexes displaying a similar phenomenon).

X-ray structural analysis of $Mg(ClO_4)_2$(**LV**) · H_2O reveals [465] that the cation is not paired with the anion and interacts with all seven oxygens of the ligand as well as with the water oxygen. Two crystallographically different Mg^{2+} ions are present in a more or less similar environment; the water molecule in each complex unit plays double action and also binds the ClO_4^- ions (Fig. 34). If the longest contact for each type of Mg^{2+} (2.49 or 2.58 Å) is also considered, then Mg^{2+} in the system is 8-fold coordinate (Table 5)—an uncommonly high coordination number for this cation. Of the M^{2+} ions, the Mg^{2+} is apparently the only one which can force charge transfer on O-sites in the MCM so that **LV** succeeds in the dehydration (except for one water molecule) of the cation through its three-dimensional approach and the associated macrocyclic effect.

(v) Category 5: macrocycles carrying non-oxygen donor(s) and those carrying oxygen or non-oxygen heterocyclic nuclei

These macrocycles which exhibit wide structural variation have been studied with the primary aim of monitoring the effect of donor atoms on the complexing ability and selectivity towards M^{z+}. One or more (or even all) oxygens of a crown may be replaced by NH, NR (R = a substituent), S or P. Also, one or more heterocyclic nuclei may be fused onto the crown ring which includes N-donor pyridine and/or O-donor furan or pyran.

For macrocycles incorporating non-oxygen donor(s), the complexing ability towards M^{z+} decreases in general in the order O > NR > NH > S [9,46]. Compared with B15C5 and 18C6 the complexing properties of **LVI** [383] and **LVII** [142] (Fig. 35) respectively are distinctly poorer; for **LVI**, the NH sites diminish the basicity of those oxygens which are away from the aryl

Fig. 35. Category 5 crown-related macrocycles (carrying non-oxygen donor(s) and those carrying oxygen or non-oxygen heterocyclic nuclei) **LVI–XC**: **LVII**, R = H; **LVIII**, R = Me; **LIX**, R = $C_{10}H_{21}$ (decyl); **LXII**, X = NH; **LXIII**, X = O; **LXIV**, R = $(CH_2)_4NH_2$; **LXV**, R = H; **LXVII**, n = 2, R = CH_2CH_2OH; **LXVIII**, n = 2, R = CH_2CONH_2; **LXIX**, n = 1, R = CH_2CH_2OH; **LXX**, n = 2, R = $CH_2CH_2CH_2NH_2$; **LXXI**, n = 1, R = Me; **LXXII**, n = 1, R = CH_2CH_2OMe; **LXXIII**, n = 3, R = $(CH_2CH_2O)_3C_8H_{17}$; **LXXIV**, n = 2, R = $CH_2CH_2OC_8H_{17}$; **LXXVII**, X = S; **LXXVIII**, X = O; **LXXXI**, R =  ; **LXXXII**, R = $(CH_2)_3$; **LXXXIX**, R = Me, X = $(CH_2)_2$; **XC**, R = H, X =  .

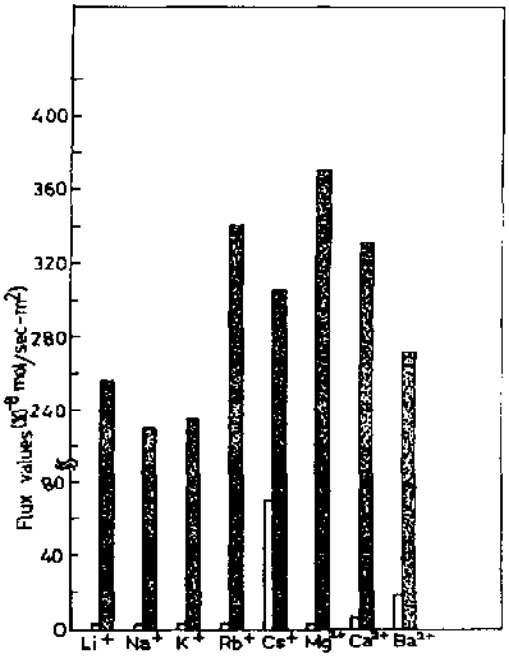


Fig. 36. Showing a remarkable competitive transport efficiency of **LVII** for Sr^{2+}.

nucleus. It would be of interest to investigate the relative donor atom preference of M^{z+} for P and in particular S but many MCM containing such donor sites have not yet been investigated.

In a variety of non-aqueous solvents such as acetone (AC), MeCN, PC and nitromethane (NM), the stability values of Li^+ with the size-mismatched **LVII** are consistently higher than those with 18C6 [466] under the same conditions. Obviously, the higher charge density Li^+ has made effective use of the polarizable sp^3-hybridized nitrogens in the MCM as would be expected to happen with any high charge density cation (Mg^{2+}, proton or even Li^+).

Substitution of oxygen donors by other donors also modifies the selectivity patterns. Thus, while the selectivity order for 18C6 (as revealed by multinuclear NMR studies) is $Cs^+ > Na^+ > Li^+$, **LVII** [466] displays a reverse selectivity order ($Li^+ > Na^+ > Cs^+$). The stability values and the selectivity pattern with these MCM are, however, a function of the solvent. Thus, **LVII** does not interact with Li^+ in DMF or in DMSO so that in such solvents Li^+/Na^+ selectivity is lost [466]. It is, therefore, not surprising that **LVII** completely fails to extract Li^+ (as pic^-) from water to dichloromethane [467], although in aprotic and not so strongly solvating solvents effective complexation of Li^+ takes place. In MeOH, **LVII** displays a K^+/Na^+ selectivity as revealed by conductance measurements whereas in MeCN the stability values for Na^+–**LVII** and K^+–**LVII** systems are comparable [468].

Unlike 18C6, **LVII** is unable to distinguish between Sr^{2+} and Ba^{2+} in MeOH [469] (log K values are 5.7 and 5.9 respectively) while in water [368] a distinction is noticeable (log K values are 2.56 and 2.97 respectively). Competitive transport investigation on Sr^{2+}–M^{z+} mixtures has, however, revealed [365] that **LVII** is efficient for Sr^{2+} over other M^{z+} including Ba^{2+} (Fig. 36). This suggests that a marginal difference in solution stability can be all important towards transport selectivity. Single-cation transport studies with **LVII** have revealed that Ca^{2+}, Sr^{2+} and Ba^{2+} are transported better than Ag^+ [353] but the competitive transport studies on Ag^+–M^{z+} mixtures have revealed that Ag^+ is transported preferably over Ca^{2+}, Sr^{2+} and Ba^{2+} [368]. Obviously, transport behaviour from single-cation studies need not correspond to that observed from the competitive transport studies.

As expected, the complexing ability of **LVIII**, which carries a methyl group on each of the two nitrogens, is higher than that of **LVII** [469]. However, the interaction behaviour of **LIX**, which contains two decyl groups, is significantly different from that of **LVII**. Competitive transport studies using **LIX** for Sr^{2+}–M^{z+} mixtures have revealed [365] that the transport of Ba^{2+} is preferred over that of Sr^{2+} while for other Sr^{2+}–M^{z+} systems the transport efficiency towards the selectively transported Sr^{2+} is much lower than that with **LVII**.

The ^{15}N NMR investigations on **LVII**, **LVIII** and related MCM have revealed [470] that M^+ mainly produce upfield shifts while M^{2+} cause mainly downfield shifts. Thus, complexation shifts are downfield with the increased charge density of M^{z+} but upfield with increasing polarizability of the cation.

LIX has been employed [357,359] for active as well as passive transport of K^+ via salts of amino-acid anions but primary attention has been on the transport behaviour of the anion.

Ligand **LVIII** displays a notable Ba^{2+} selectivity towards synthesis of solid complexes [471] over similar-sized K^+. X-ray structural analysis of the complex KNCS(**LVII**) reveals [472] that the K^+–N distances (2.86 Å) are slightly longer than the K^+–O distances (2.83 Å) and the anion maintains a very weak contact (3.33 Å) with K^+. While 18C6 discriminates between K^+ and Rb^+ (yielding 1 : 1 [153] and 2 : 2 [181] complexes respectively for NCS^- as counter-anion), **LVII** interacts with Rb^+ [473] in a manner similar to K^+.

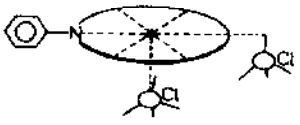


Fig. 37. A schematic view of $NaClO_4$(**LXI**).

With **LX** [474], which can be considered to be **LVII** with a terphenylophane bridge introduced between the two nitrogens, the anionphilic Na^+ can be charge separated from NCS^- in the complex [Na(**LX**)]NCS · MeOH [475] (Table 5). The contribution of NCS^- stabilization through bonding with MeOH and an adequate polarizability of nitrogen atoms by the not so low charge density Na^+ should be important towards this type of interaction. The related **LXI**, which carries only five donor sites, displays stronger ion pairing of the anion (ClO_4^-) with the cation in the complex $NaClO_4$(**LXI**) [476] (Table 5) than is possible in the complex $NaClO_4$(B15C5) [138]. The anion in the former complex interacts more strongly through one oxygen (2.39 Å) and through chlorine of the second ClO_4^- from an adjoining molecule (2.65 Å) (Fig. 37) whereas, in the latter, ClO_4^- is bidentate through the two oxygen atoms (2.43 and 2.63 Å). Since the ring nitrogen is directly in mesomeric interaction with the phenyl nucleus, the role of nitrogen should be considerably shifted towards the role of oxygen so that in its complexing ability **LXI** should not be so different from B15C5. The different bonding mode of the ClO_4^- ions is related to the lattice.

Some data for macrocycles containing –N=N– azo group(s) are available [477–479] but the main aim of the work has been towards the cis–trans relationship of the ligands rather than towards their discriminating ability for M^{z+}.

Macrocycles containing a majority of nitrogen donors are particularly attractive for M^{2+}. Compared with 18C6, the all-nitrogen donor **LXII** shows a preference for Ca^{2+} over K^+ in water [480]. The specificity for Ca^{2+} over K^+ (and Na^+ as well as Mg^{2+}) is retained even if there are five nitrogens along with an oxygen as in **LXIII** [481]. However, **LXIV** is unique in that it shows [481] complexation with Mg^{2+} only, while towards Ca^{2+}, Na^+ and K^+ it is non-interacting. The role of the side-arm in **LXIV** is important because the analogous macrocycle (**LXV**), which is devoid of the side-branch, is non-interacting [481] towards all four cations. Such macrocycles interact [482] with nucleotide complexes of Mg^{2+} and Ca^{2+} to yield ternary complexes.

Incorporation of one or more nitrogen atoms into the crown ring provides an opportunity for attachment of flexible side-arms with donor atoms. Such "nitrogen-pivot lariat ethers" [483] received attention [484,485] regarding their interaction with M^{z+} even before the term "lariat ethers" was introduced [403]. **LXVI**, for example, is known to be strongly complexing towards Na^+ in 90 vol.% MeOH–10 vol.% H_2O [483]. The total number of oxygens in the MCM is more important [486] than those present in the ring; moreover the binding of Na^+ is maximum when a total of six oxygens is present. As revealed by measurements of ^{13}C NMR relaxation times and ^{23}Na line widths [487], N-pivot lariat ethers are more dynamic complexing

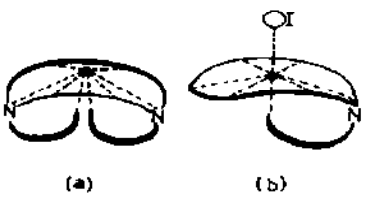
agents than the corresponding C-pivot compounds. These results [487] and the potentiometric studies [488] have also revealed that the side-arm contributes significantly to cation binding.

N-pivot lariat ethers have drawn considerable attention for selectivity studies. **LXVII** [489] is selective for Ca^{2+} over Na^+, K^+ and Mg^{2+} [490] but the selectivity for Ca^{2+} over these cations is enhanced for **LXVIII**, obviously, because of a more effective contribution of the side-arms in the latter. The selectivity for Ca^{2+} over Li^+, Na^+ and K^+ is observed even with a much smaller ligand (**LXIX**) [485]. This strengthens the ideology that ion–cavity size is hardly important for the selectivity patterns. Incidentally, **LXIX** resembles **LXVII** in the nature of the side-arms but shows a much higher log *K* value for Ca^{2+} (6.9) [485] than found for **LXVII** (4.08) [490]. **LXIX** binding has also been studied by following ^{43}Ca NMR [491].

Macrocycle **LXX** [467] demonstrates that an unusually high complexing efficiency results in a loss of selectivity. This is possibly because the side-chains of **LXX** contain primary amino groups which are of appropriate length, and the quantitative extraction of each of Li^+, Na^+ and K^+ (as picrates) becomes possible.

Until recently, most publications focused on the role of the side-arm towards ion-binding strength while its role in modifying the interaction stoichiometry has recently been demonstrated [492]. Thus, **LXXI** displays a 1 : 2 interaction with Na^+ whereas **LXXII** forms a 1 : 1 complex with the same cation and for **LXIX**, 1 : 2 complex formation is altogether suppressed. Such a change of interaction stoichiometry is possible because just one molecule (**LXIX** or **LXXII**) can meet the required coordinative saturation. Extensive screening of various ligands from this viewpoint is, in fact, desirable to rationalize the role of the side-arm(s).

Electrically neutral N-pivot lariat ethers can be successfully used to mediate active (up-hill) transport through planned control on the environment of the source and the receiving phases. Taking advantage of a remarkable difference in the M^+-complexing ability of these ligands under basic and



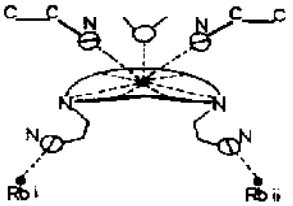


Fig. 38. A schematic view of (a) [Na(**LXVII**)]I and (b) KI(**LXVI**).

Fig. 39. A schematic view of [Rb(**LXXV**)(H_2O)]I.

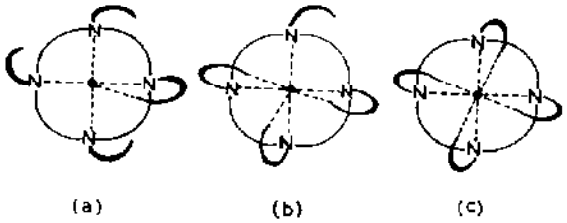


Fig. 40. A schematic view of M^+–**LXXVI** complexes: (a) $[Li_2(\mathbf{LXXVI})(H_2O)]Cl_2.H_2O$ (only one moiety shown); (b) [Na(**LXXVI**)]NCS; (c) [K(**LXXVI**)]NCS.

acidic conditions (which is strong and poor respectively), Matsushima et al. devised [493] a three-phase active transport system with a basic source phase and an acidic receiving phase; **LXXIII** displayed highly selective K^+/Na^+ active transport while **LXXIV** offered marginal Na^+/K^+ selectivity.

X-ray diffraction analysis (Table 5) of KI(**LXVI**) and [Na(**LXVII**)]I [494] has revealed that in either complex the side-arm(s) participate in cation binding (Fig. 38). It will be interesting to examine how the solid state interaction pattern of **LXVII** is directed towards Ca^{2+} for which it is much more selective in solution than say Na^+ [490]. The inflexible $-CH_2CN$ side-arms in **LXXV** interact in a different way in the complex $[Rb(\mathbf{LXXV})(H_2O)]I$ [495]. Instead of binding the same cation with which the crown ring is coordinated, they interact (Fig. 39) with two different cations from adjoining molecules; the Rb^+–N(CN) contacts are longer (3.34 and 3.36 Å; Table 5) than the Rb^+–N(ring) contacts (3.16 and 3.24 Å).

Macrocycle **LXXVI** [496] carries a side-arm on each nitrogen atom of the ring. X-ray diffraction analysis [496–498] of its Li^+, Na^+ and K^+ complexes reveals (Fig. 40) an interesting gradation. The complex with LiCl is 2 : 1, viz. $[Li_2(\mathbf{LXXVI})(H_2O)]Cl_2 \cdot H_2O$ [497] while those of NaNCS [498] and KNCS [498] are each 1 : 1. None of these three complexes displays pairing of the complexed cation with the anion. The Li^+ complex is not bimetallic in the true sense of the term. Although one Li^+ is penta-coordinated with four ring nitrogens along with one side-arm (Fig. 40), the other monohydrated Li^+ involves coordination through three side-arms from three different molecules to acquire a tetra-coordinated state. In the complexes [Na(**LXXVI**)]NCS and [K(**LXXVI**)]NCS, wherein charge separation has taken place, the arms participating in binding of the cation are three and four respectively (Fig. 40).

Solution studies (^{13}C NMR) of the interaction of **LXXVI** with M^+ have revealed [499] that the number of side-arms involved in coordination with Na^+ continues to be three but for Li^+ and K^+ it is between two and three respectively; the solvent competes for interaction with the cation as well as for the side-arm(s).

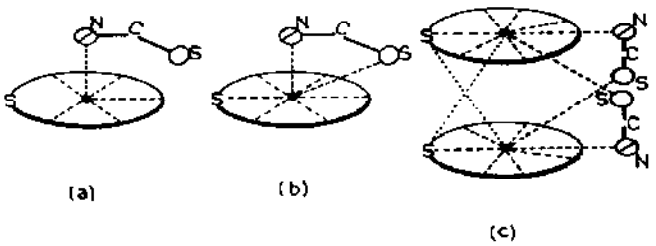


Fig. 41. A schematic view of M^+–**LXXVIII** complexes: (a) NaNCS(**LXXVIII**); (b) [K(**LXXVIII**)]NCS; (c) [RbNCS(**LXXVIII**)]$_2$.

Substitution of oxygen by sulphur results in a drastic decrease in the complexing ability, as indicated by solution studies on **LXXVII** [142] (see also ref. 500). The decrease in the stability is even greater than that for the corresponding nitrogen analogue **LVII**. This observation is in accordance with the fact that sulphur is a softer donor than nitrogen. This trend has been confirmed by subsequent studies of **LXXVIII** [245] and **LXXIX** as well as **LXXVII** [235, 501]. It is further observed [501] that the decrease in stability of the complex with thia-ligands is only marginally dependent on the nature of the solvent but varies significantly with the nature of the cation (Li^+, Na^+ and Cs^+), the change being the largest for Cs^+. The sulphur macrocycles have a limitation in that the sulphur-pivot lariats cannot be devised. Some chemically "switched-on" macrocycles containing a dithia-linkage have recently been introduced [502] but their M^+-extracting ability is much less than that of the analogous crowns.

The complexing behaviour of **LXXVIII** in the solid state has been examined for Na^+ [503], K^+ [504] and Rb^+ [505] employing NCS^- as the counter-anion (Fig. 41). Using this MCM, an interesting difference is that for Na^+, the sulphur atom does not interact while for K^+ or Rb^+ it interacts, though weakly. The Rb^+ complex is, however, dimerized through NCS^- ions, uniquely in that the N of the anion binds one Rb^+ while S binds the other. The neutral ring S is also possibly involved (Rb^+–S, 3.47 Å) in dimerization (Fig. 41(c)). The S-affinity is enhanced from Na^+ to Rb^+; Na^+ does not appear to interact even with the anionic S of NCS^- while Rb^+ tends to interact even with the neutral S of the adjoining ring.

A correlation of molecular conformation with the thermodynamic stability of M^+–**LXXVIII** complexes has been attempted [506]. Thia-macrocycles possessing various substituents on an aromatic moiety have also been investigated but the primary aim was to assess the coordinating ability of the intra-annular functional groups [507,508] rather than to assess the role of the sulphur atoms.

The donor properties of phosphorus towards M^{z+} have not been seriously explored. Some phosphorus-containing macrocycles have been investigated

[509–512] but they do not appear to show behaviour superior to that of crowns. Apparently, P may act more as a site for further substituents than as an effective donor for M^{z+}.

Macrocycles incorporating O-based [513–518] or N-based [21,519–533] heterocyclic nuclei have been examined. **LXXX**, although it possesses the same number of oxygens as 12C4, is more highly selective for Li^+ (96% extraction) [513]. The difference is perhaps because of a diminished solvation of **LXXX** and a superior coordinating ability of the furanyl oxygens. However, **LXXX** selectively transports Na^+ (instead of Li^+) [513] which may be because the Li^+–**LXXX** complex is too stable to be released from the membrane into the receiving phase.

With **LXXXI**, Ba^{2+} yields 1 : 2 complexes for BPh_4^-, ClO_4^- or even NCS^- while other M^{z+} (Na^+, K^+, Ca^{2+} and Sr^{2+}) form 1 : 1 complexes [516]. X-ray structural analysis of $[Ba(\mathbf{LXXXI})_2](BPh_4)_2$ reveals [516] it to be a genuine charge-separated sandwich wherein for each ligand molecule, only one of the four Ba^{2+}–N contacts is short enough to be compared (2.96 Å) with the two Ba^{2+}–O contacts (2.92 and 3.02 Å). With **LXXXII**, which contains two flexible linkages between the four nitrogens, Ba^{2+} forms 1 : 1 as well as 1 : 2 complexes [517] which can be prepared by the template method and a metathetical reaction respectively. X-ray structural analysis of $[Ba(\mathbf{LXXXII})_2(H_2O)_2][Co(NCS)_4]$ reveals [517] Ba^{2+} to be enclosed within an "incomplete sandwich". One ligand molecule provides all the six donors for coordination and the other molecule provides only one furanyl oxygen and two nitrogens while the other three atoms are folded out giving the two water molecules an opportunity to coordinate with the cation. The macrocycle **LXXXIII**, with too many oxygens over nitrogens, fails to cause separation of the anion from the comparatively anionphilic Sr^{2+} in the complex $Sr(NCS)_2(\mathbf{LXXXIII}) \cdot H_2O$ [518] and the two NCS^- ions coordinate the cation from the same axial side.

Although heterocyclic moieties such as phenanthroline [529,530] and pyrazole [531,532] have been incorporated in the donor rings, pyridine is the most common nucleus [519–528,533]. We consider these MCM to be of value towards the delineation of the chemistry of divalent cations. Incorporation of a pyridine moiety in place of an oxygen results in decreased stability of the complexes with M^+ or larger M^{2+}. Nevertheless, the pyridine nitrogen is a better donor than a normal nitrogen. The ligand **LXXXIV**, for example, interacts with M^{z+} almost as strongly as 18C6 [245,520].

X-ray structural analysis of $[Mg(\mathbf{LXXXV})(H_2O)_2]Cl_2 \cdot 4H_2O$ reveals [519] coordination of only two out of the available six water molecules in the lattice with Mg^{2+} while the MCM offers all five donors. The cavity of the MCM is rather large for the Mg^{2+} ion so a thorough interaction of the ring donor sites should be more a consequence of the N-philicity of this high charge density cation.

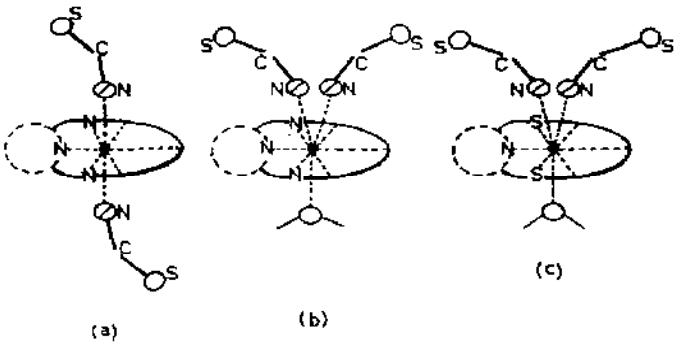
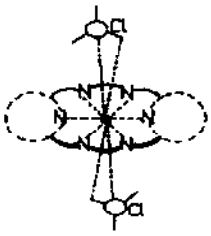


Fig. 42. A schematic view of (a) $Ca(NCS)_2$(**LXXXVI**); (b) $M(NCS)_2$(**LXXXVI**)$\cdot H_2O$ (M^{2+} = Sr^{2+} or Ba^{2+}); (c) $Ba(NCS)_2$(**LXXXVII**)$\cdot H_2O$.

X-ray structural analysis of the $Ca(NCS)_2$, $Sr(NCS)_2$ and $Ba(NCS)_2$ complexes of **LXXXVI** reveals [525] a distinct difference in the chemistry of Ca^{2+} compared with that of Sr^{2+} and Ba^{2+}. The two NCS^- ions interact with Ca^{2+} from two opposite directions suggestive of a transitory ionization of the Ca^{2+}–NCS^- bond. Forced charge transfer on the lone pair of a donor nitrogen by a cation (self-complexation) is enhanced with the charge density of the latter. Since half the donor sites of **LXXXVI** are nitrogens, interaction of Ca^{2+} is expected to be stronger than for Sr^{2+} or Ba^{2+}. Transitory ionization of $Ca(NCS)_2$ during complexation and distribution of one NCS^- on each axial side is, therefore, understandable. However, weakly self-complexing Sr^{2+} and Ba^{2+} appear to complex as undissociated ion pair (Fig. 42) and the anions interact with the cation from the same axial side while the unoccupied axial position is filled with water. X-ray structural analysis of $Ba(NCS)_2$(**LXXXVII**)$\cdot H_2O$ [526] presents an analogous situation; the pyridine N interacts more weakly than the N atoms of the NCS^- ions. (It should be noted that self-complexation on the O-donor is relatively difficult because of the enhanced electronegativity of O, so that self-complexation is unfavourable even for Ca^{2+} and appears to be effective only for Mg^{2+} as mentioned [9,11] for the complexes of B15C5.)



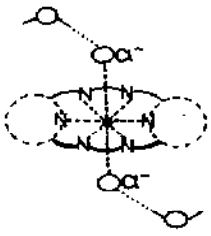


Fig. 43. A schematic view of $Ba(ClO_4)_2$(**LXXXVIII**).

Fig. 44. A schematic view of [$SrCl_2$(**LXXXIX**)]$\cdot 2H_2O$.

Ba^{2+} yields a 1 : 1 complex with **LXXXVIII**. X-ray structural analysis of $Ba(ClO_4)_2$(**LXXXVIII**) reveals [523] that the Ba^{2+} is 10-coordinate through six nitrogens from the MCM and four oxygens from the two ClO_4^- anions. Ion pairing appears to occur because of highly inadequate coordinative saturation provided by the ligand (Fig. 43). Ionization of $Ba(ClO_4)_2$ during complexation and distribution of the ClO_4^- ions one on each side is at least in part related to a weakly pairing ability of ClO_4^- compared with that of NCS^- in, for example, $Ba(NCS)_2$(**LXXXVI**) · H_2O.

Although Cl^- in [$SrCl_2$(**LXXXIX**)] · $2H_2O$ is highly cation pairing, X-ray analysis [521] has shown that one Cl^- is distributed on each axial side of the ring complexing the cation (Fig. 44). The necessary ionization during complexation for this system appears to owe more to the polar protic media (moist methanol) used for the synthesis of the complex to which Cl^- can be visualized to force a bond during complexation of the counter-cation. Structure results indeed show that each Cl^- ion, which ultimately pairs with the complexed cation, is bonded with a molecule of water (Fig. 44). With **XC**, wherein polarizability of four of the six ring nitrogens is severely inhibited by the fused benzo nuclei, Ca^{2+} (and Sr^{2+}) become unfavourable cations. Consequently Ba^{2+} yields 1 : 2 complexes [522] while Ca^{2+} and Sr^{2+} form 1 : 1 species. This situation is analogous to the one for **LXXXI** [516] in which also the benzo nuclei are exercising the same acidic effect on four ring nitrogens.

(vi) Category 6: macrocycles carrying oxo- and amide-substituents with or without heterocyclic nuclei

Macrocycles of this category are important because they ensure substantial modification of the complexing properties of the crown ring. Compared with 18C6, for example, the complexing potential of **XCI** and **XCII** (Fig. 45), each of which carries a pair of carbonyl oxygens directly attached to the crown ring, is drastically reduced [244,534]. This is so because orientation of the carbonyl oxygens is not suited for cooperative interaction of the ethereal oxygens with M^{z+} and because electron-withdrawing carbonyls deplete the basicity of the adjacent ethereal oxygens.

The complexing ability of **XCII** is diminished compared with that of **XCI** [244], obviously because enlargement of the ring in **XCII** is more important than the increase in the number of ethereal donors. The macrocycle **XCIII** shows [520,534,535] a much higher complexing ability than **XCI**. Nevertheless, the complexing ability of **XCIII** is less than that of the corresponding macrocycle, **LXXXIV**, without carbonyl functions [245,520]. A pronounced carbonyl effect is noticed in **XCIV** [535] which is non-complexing (towards Na^+, K^+ and Ba^{2+} in MeOH), for in the same medium, **LXXVIII** displays

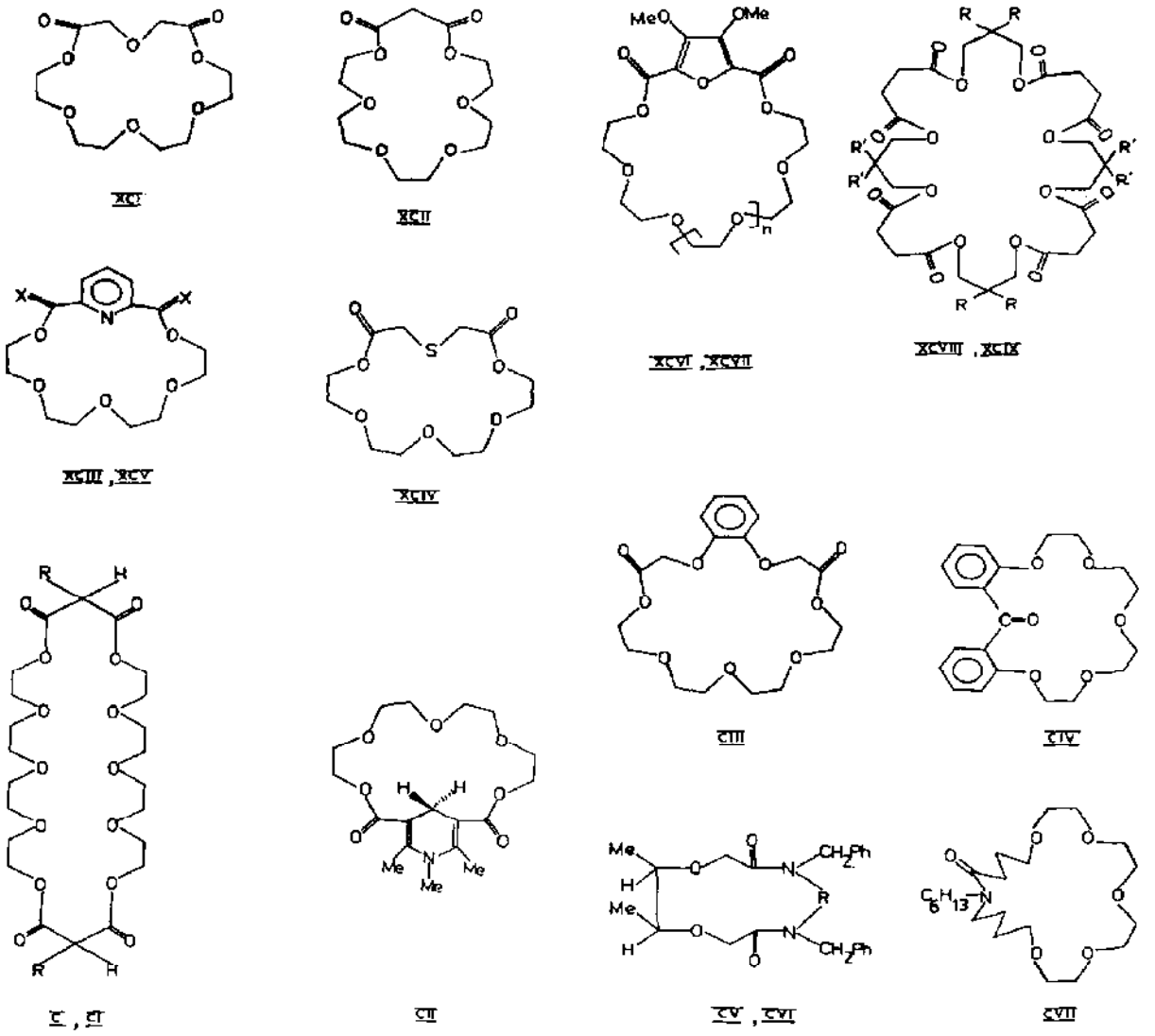


Fig. 45. Category 6 crown-related macrocycles (carrying oxo- and amide-substituents with or without heterocyclic nuclei) **XCI–CVII**: **XCIII**, X = O; **XCV**, X = S; **XCVI**, $n = 1$; **XCVII**, $n = 2$; **XCVIII**, R = H, R′ = Me; **XCIX**, R = R′ = Me; **C**, R = n-C_8H_{17}; **CI**, R = n-$C_{12}H_{25}$; **CV**, R = $CH_2(CH_2OCH_2)_3CH_2$; **CVI**, R = $(CH_2)_{12}$.

complexing ability (log K values for Na^+, K^+ and Ba^{2+} being 2.57, 3.61 and 3.4 respectively [245]).

In addition to solution stability, incorporation of the carbonyl functions has a bearing on selectivity. Although the selectivity sequence for 18C6 (viz. $Ba^{2+} > K^+ > Na^+$) is maintained by **XCI** [244], it is modified to $K^+ > Na^+ > Ba^{2+}$ for **XCII** [244]. However, the K^+/Na^+ selectivity of **XCI** is lower than that of 18C6. Furthermore, the selectivity sequence for **XCIII** is

$K^+ > Ba^{2+} \sim Na^+$ [520] and its complexing ability is high but its cation discriminating ability is feeble.

As expected, replacement of carbonyl groups with thiocarbonyl groups results in a reduced complexing ability as noted for **XCV** compared with **XCIII** [536], for example. Model membrane transport work with **XCVI** and **XCVII** has revealed [537] an interesting Cs^+/Rb^+ selectivity (about 6-fold for each). Study of the substituent effects on **XCIII** and the related analogues [538] and later work [534] revealed that for Na^+, K^+, Cs^+, Ca^{2+} and Sr^{2+} (but not for Rb^+) the transport rate decreases in the order OMe > H > Cl.

Both **XCVIII** and **XCIX** possess a 36-membered ring. They are unique in that, despite their large cavity, they preferentially extract Li^+ and Ca^{2+} respectively [539]. This is not easily understandable, unless the symmetrically distributed carbonyl functions rotate all the way inward to bind the cation as noted for the nactins [9]. The ion transport ability of **XCIII** and the related molecules, possessing a long alkoxy-substituted pyridine subcyclic unit, has been investigated for the Ag^+–K^+ and Ag^+–Cs^+ mixtures; transport of Ag^+ is preferred [540]. Macrocycles **C** and **CI** do not effectively complex K^+ but display transport selectivity towards this cation [541].

A variety of other macrocycles carrying carbonyl groups have been examined [542–548] but their detailed cation-discriminating ability has not been explored. It has, however, been established that dioxo-macrocycles possess weaker complexing ability than the mono-oxo-macrocycles [548].

The X-ray structural analysis of the $NaClO_4$–**CII** complex has revealed [549] that Na^+ is paired with ClO_4^- and also coordinated with a molecule of acetone. However, complete details of cation coordination are not described, the emphasis in the publication being on the ligand conformation.

The X-ray structural analyses of the KNCS complexes of **XCI** [550], **XCIII** [551], **CIII** [552] and **CIV** [553] have been carried out and a comparison of the complexing behaviour of these macrocycles can be made. In the complexes of **XCI, XCIII** and **CIII**, the carbonyl oxygens are non-interacting, while in the **CIV** complex it interacts intramolecularly and intermolecularly (Fig. 46). Obviously, the carbonyl oxygen is happily suited for complexation towards M^{z+} but for the former trio of ligands, the conformational juxtaposition of $>C{=}O$ ends is unsuitable for a cooperative interaction with ethereal oxygens. All the complexes are ion paired (Table 5) which is in contrast to, say, [K(18C6)]NCS [153] (Section B (ii) (b)). The difference for KNCS–**XCI** [550] and KNCS–**XCIII** [551] from the other two complexes is that the cation is in contact with two anions through N as well as S (Fig. 46); the $K^+ \cdots NCS^-$ distance in the latter complex is longer than even the K^+–N(pyridine) distance. Both the observations indicate that ion pairing for these two complexes is imposed on the low charge density K^+. Each cation

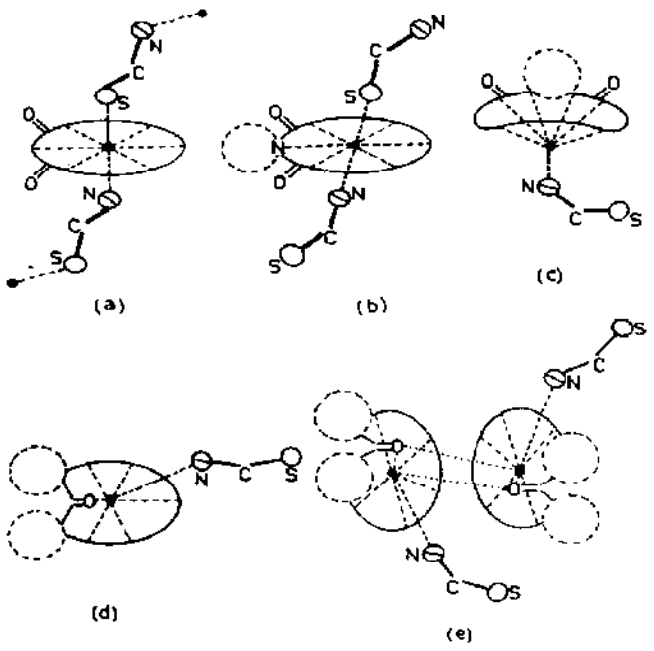
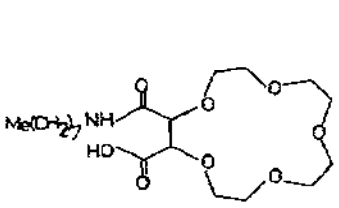


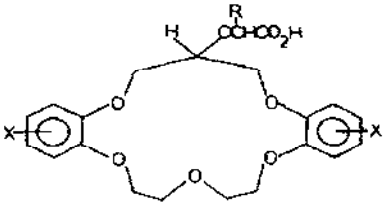
Fig. 46. A schematic view of the KNCS complexes of (a) **XCI**; (b) **XCIII**; (c) **CIII**; (d) **CIV** (1 : 1 moiety); (e) **CIV** (2 : 2 moiety).

in the 1 : 1 as well as 2 : 2 moieties of the KNCS(**CIV**) complex is bound to all the ring donor atoms including the carbonyl ring oxygen and the NCS^- anion. The $>C{=}O{-}K^+$ contact in the 1 : 1 species is stronger (2.59 Å) and intramolecular, while in the 2 : 2 species it is intramolecular as well as intermolecular and relatively longer (2.85 and 3.05 Å); it is the interlink with the latter moiety (Fig. 46) through which dimerization takes place.

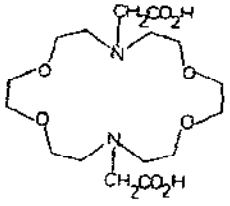
Petranek and Ryba [554] noted that the macrocycles carrying amide group(s) in the ring are particularly suitable for complexation of M^{2+} ions. Subsequent investigations [555–560] yielded useful results. **CV** displays a selectivity for Ca^{2+} over Ba^{2+} and M^+ [556] but this selectivity is lost in **CVI** which possesses the same number of amide groups but a lesser number of ethereal oxygen atoms. Interestingly, each of **CV** and the related macrocycles forms a 1 : 2 complex (in situ generation) for tetra(4-chlorophenyl)borate as the self-stabilized counter-anion [557]. Ca^{2+} is extracted from the aqueous phase much more efficiently into nitrobenzene by **CV** than any of Li^+, Na^+, Mg^{2+}, Sr^{2+} and Ba^{2+} [558]. However, an MCM containing amide group(s) is not always Ca^{2+} selective, for **CVII** shows [560] a much higher Ba^{2+}/Ca^{2+} extracting ability; this may be attributed to a dominant ether-to-amide donor atom ratio.



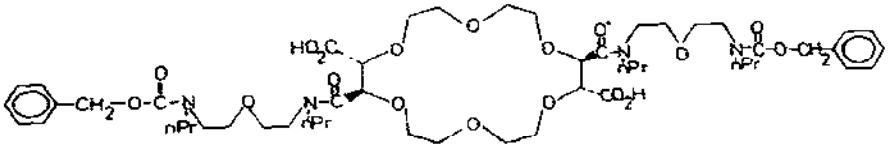
CVIII



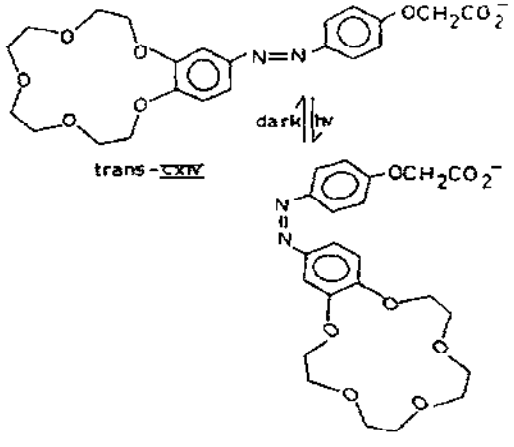
CIX - CXI



CXII



CXIII



trans - CXIV

cis - CXIV

Fig. 47. Category 7 crown-related macrocycles (anionic macrocycles) **CVIII–CXIX**: **CIX**, $R = X = H$; **CX**, $R = (CH_2)_7Me$, $X = H$; **CXI**, $R = H$, $X = C(Me)_3$; **CXVIII**, $R = NO_2$; **CXIX**, $R = CF_3$.

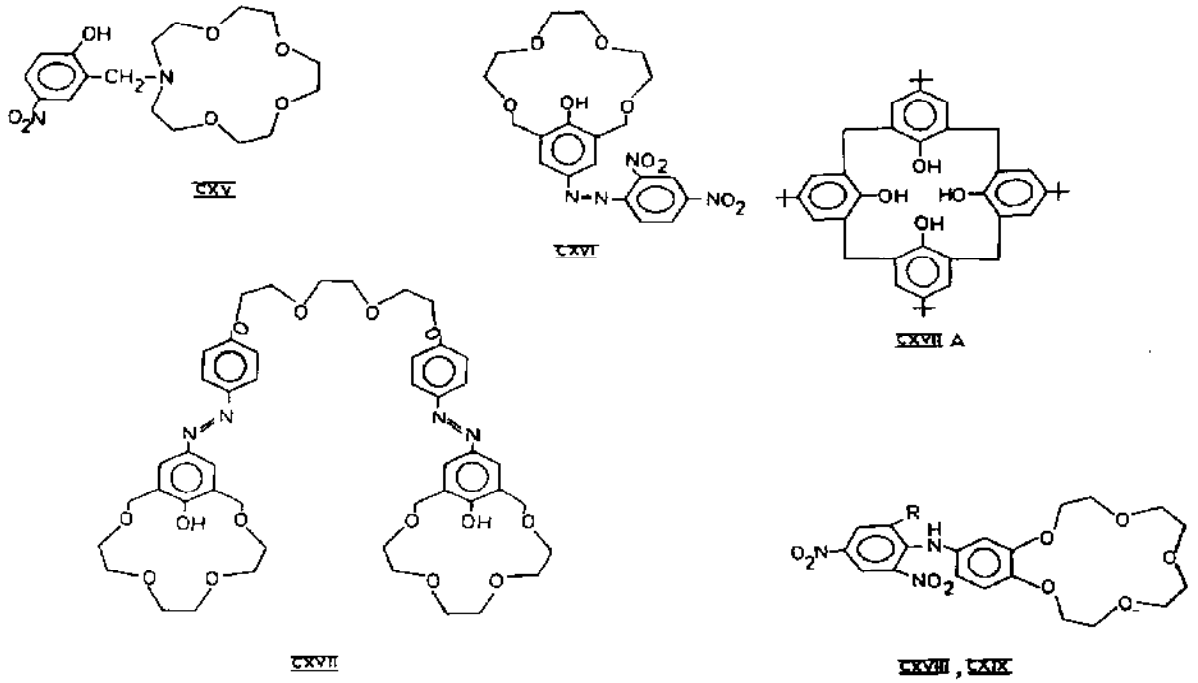


Fig. 47. (continued).

(vii) Category 7: anionic macrocycles

The chemistry of anionic macrocycles is different from that of the electrically neutral ones. They not only have to provide the coordination environment but also to act as charge neutralizers. Helgeson et al. [561] and Ungaro et al. [427] used the anionic macrocycles during the initial development of the subject. Fyles and coworkers employed [562–564] functionalized crowns such as **CVIII** (Fig. 47) for the transport of M^+ across chloroform against the concentration gradient (from the basic source phase to the acidic receiving phase coupled with counter-transport of protons). Anionic carriers derived from 18C6 transport K^+ selectively and all the other cations more rapidly than the analogous 15C5 derivatives which are Na^+ selective [564].

Bartsch and coworkers [565–575] have extensively investigated the interaction properties of the anionic macrocycles towards M^{z+}. The extraction efficiency of the anionic macrocycles, say **CIX**, towards a cation is insensitive to the change of the counter-anion (from Cl^- to SO_4^{2-}) [565] suggesting that the counter-anion is not transferred to the organic phase during extraction. It also indicates that the macrocycle interacts as an anion. Obviously, in order to make use of its transferring ability, it is essential that the macrocycle be kept confined into the organic phase. This can be achieved by incorporating an appropriate lipophilic group, as in **CX** [567] so

that the contribution of the anionic group towards polarity can be compensated. Ionization of the anionic macrocycle in the non-polar phase, which may otherwise appear rather impossible, is greatly aided by the affinity of the anionic group of the macrocycle towards M^+.

CXI is interesting with regard to extraction, as well as transport, in that it exhibits complete rejection of Li^+ and a high Na^+/K^+ preference [570]. **CX** displays [567] an extraction selectivity in the order $Na^+ \geqslant K^+ > Li^+ \geqslant Rb^+ > Cs^+$ wherein the extraction of Li^+ is significant. For the liquid emulsion as well as for bulk liquid membrane transport, using the same macrocycle, the selectivity orders are, however, $Na^+ > K^+ > Rb^+ > Cs^+$ and $K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$ respectively [573].

The nature of the non-polar phase is apparently more important for the anionic macrocycles than for the electrically neutral analogues. Using **CXI** in the competitive transport investigations, the cation-loading capacity of the organic phase is reduced by 60% when chloroform is replaced by toluene [571]. The selectivity order ($Na^+ \gg K^+ > Rb^+ \sim Cs^+ > Li^+$) in chloroform is modified to $Na^+ > Li^+ \sim K^+ > Rb^+ > Cs^+$ for toluene [571]. Another important conclusion from the studies is that the results of competitive extraction [565,566] as well as competitive transport [568] need not be extrapolated towards those of single-cation studies as the selectivity orders in the two types of studies can be conspicuously different.

^1H NMR spectroscopic studies on the anionic macrocycles containing two carboxylic groups have revealed an interaction towards M^{2+} [576], so much so that **CXII** can cause an insoluble salt such as $BaSO_4$ to be soluble in water [577].

Anionic macrocycles are in general M^{2+}/M^+ selective [578]. The lipophilic dicarboxylic acid–dicarboxamide macrocycle, e.g. **CXIII**, is expected to be doubly ionized at pH 7 and above. In this form, the binding and extraction of one M^{2+} through chelation is preferred to those of two M^+ ions independently so that the M^{2+}/M^+ transport selectivity is understandable. Indeed, at pH 8.6, **CXIII** exhibits a 12-fold Ca^{2+}/K^+ selectivity. With a decrease in the pH of the system, the doubly ionized state of the macrocycle is expected to be progressively converted into the monoanionic form which should result in a preferential uptake of M^+ over M^{2+}. At pH 2, **CXIII** displays a 200-fold K^+/Ca^{2+} transport selectivity. Likewise, a macrocycle containing an amino as well as carboxylate groups is susceptible to protonation at both sites so that controlled protonation becomes a vital factor towards its transport selectivity [579].

The phenomenon of photo-isomerization has also been incorporated in the anionic macrocycles, as in the bis-crowns. The photoisomerized *cis*-**CXIV**, for example, extracts K^+ more efficiently and selectively than the *trans*-**CXIV** [580].

The phenolic group has also been investigated as an anionic site. In contrast to **CVIII** and **CIX–CXI**, each of which possesses five donor atoms in the ring and rejects Li^+, **CXV** displays an unusual selectivity towards Li^+ [581]. This could partly be because interaction of the charge-localized phenoxide towards the high charge density Li^+ is stronger than that with the charge-delocalized carboxylate group.

Anionic chromogenic crowns [582–586] and related macrocycles [414,587,588] have evoked interest. The "crowned" dinitrophenylazophenol **CXVI** shows an Li^+-dependent characteristic colouration [583] so that a spectrophotometric method for the determination of Li^+ with **CXVI** can be devised [584]; there is some interference from K^+, Rb^+ and M^{2+} but not from Na^+ in the determination. The Li^+ colouration develops best using $CHCl_3$–DMSO–Et_3N as medium but if DMSO is replaced with MeOH, the colour development is best for Rb^+ and Cs^+ [586]. Anionic bis-crowns such as **CXVII** [589] may prove interesting in due course.

Calixarenes [367,590], represented by say **CXVII A** [367], constitute an important group of anionic macrocycles but differ from a crown-based anionic macrocycle in that there is no incorporated ethereal oxygen. They exchange their proton with a cation during complexation and thus provide a means of coupling cation transport to the reverse flux of protons. Surprisingly, however, these MCM display M^+ transport for the tight ion pairing and nucleophilic OH^- while no transport is possible for the charge-delocalized NO_3^- [367]. It may be linked in part to the preferred formation of water (interaction of OH^- and H^+) over that of nitric acid (interaction of NO_3^- and H^+). The calixarenes display a unique transport selectivity for the lowest charge density Cs^+; **CXVII A** displays the highest Cs^+/M^{z+} transport selectivity [367].

Macrocycles containing an amino group [591–594] such as **CXVIII** [594] behave as high pK_a acids (HL) through deprotonation of the –NH– group; each anion so produced is prone to undergo homoconjugation with a molecule of the parent undissociated molecule to form $[L,HL]^-$. The latter is, however, possible only for the low charge density cations K^+, Rb^+ and Cs^+ [175], which are extracted as ML, HL. The medium charge density Na^+, which holds L^- more effectively, is extracted as ML, HL plus ML. The highest charge density Li^+ yields the most strongly paired ML and does not allow L^- to undergo homoconjugation so that extraction of the salt does not take place [591]. Macrocycle **CXIX** can be used to extract 5–700 ppm of K^+ in the presence of 3000 ppm of Na^+ [593]. Since deprotonation of the macrocycle substituent and its consequent homoconjugation are the main processes involved in complexation and extraction, the pronounced pH dependence of the work medium is understandable.

(viii) Category 8: polymer macrocycles

Polymer macrocycles may be linear or net-work. They carry crowns or other macrocycles on the backbone or as pendants. The cation-binding properties of these macromolecules have been reviewed earlier [55,57,595,596] while newer information is described here briefly.

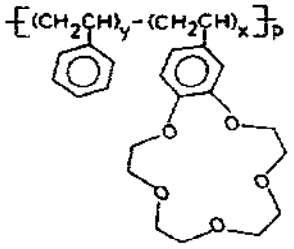
Kopolow et al. in 1971 introduced polymer macrocycles derived from 4′-vinylbenzo-15-crown-5 and 4′-vinylbenzo-18-crown-6 [597]. Now a considerable amount is known about them [598–624]. Studies include evaluation of the cation-binding properties of molecules involving side-chains such as polystyrenes [597–599], polymethacrylates [599,600], polypeptides [601] and polyethyleneimines [602,603] which greatly regulate their complexing behaviour.

In general, polymer macrocycles are distinctly more efficient in complexation than their corresponding monomeric analogues [55,441] or even the bis-crowns [433,440]. A polymer such as **CXX** (P15C5, Fig. 48) can form a 1 : 2 sandwich with a large cation such as K^+ more easily and effectively than B15C5 or B18C6. This is subject to the condition that the distance between the crown moieties on the polymer chain permits the intramolecular cooperation of the two rings. In this regard, **CXXI** (20% SP15C5) is more effective [299] than **CXX**, which is understandable because insertion of a large cation in the former with less crowding is easier. Studies on polypeptide-based **CXXII** have revealed [601] that 1 : 2 sandwich complexation is possible even if the polymer is rigid (and helical) as is a polypeptide. This observation has led the researchers to conclude that [601] the flexibility of the polymer chain is not an essential requirement for a cooperative cation binding. The validity and versatility of this conclusion calls for a more detailed examination.

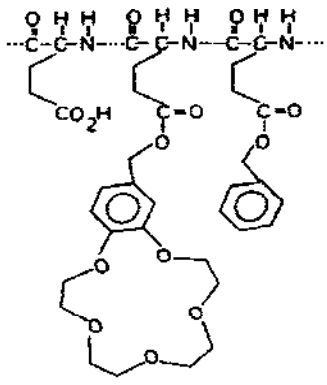
In the case where macrocycle rings are incorporated into the backbone of the polymer, the complexing ability is noticeably modified. Polymer **CXXIII**, for example, displays a poor binding ability towards Na^+, while for K^+, the binding ability is comparable only to the monomeric analogue [608]. Despite these restrictions, Ba^{2+} succeeds in forming a 1 : 2 sandwich [609] with **CXXIV** in water. This role should parallel the optimum self-encapsulating ability of Ba^{2+} [9,11] which enjoys a complementary contribution from ligand encapsulation.

With respect to the pendant polymers, the structure of the polymer influences the complexing ability of a backbone polymer. While efficient complexation can be observed for polyesters [610], backbone polymers possessing a polyamide structure display poor binding ability.

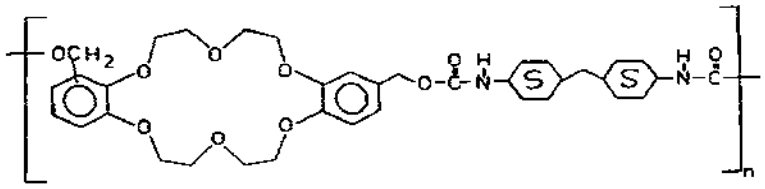
Although extraction as well as transport measurements are two convenient modes of evaluating the M^{z+} interaction patterns, disparity in the



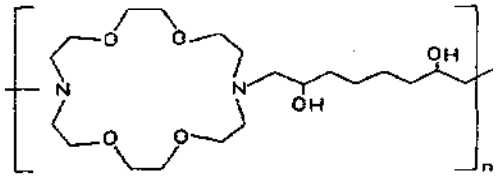
CXX , CXXI



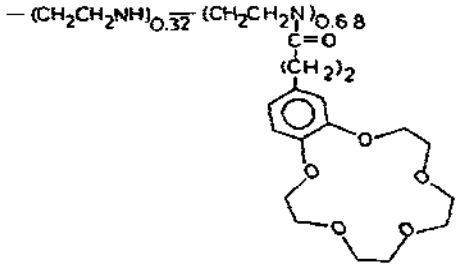
CXXII



CXXIII



CXXIV



CXXV

Fig. 48. Category 8 crown-related macrocycles (polymer macrocycles) **CXX–CXXV**: **CXX**, $x = 1$, $y = 0$; **CXXI**, $x = 0.2$, $y = 0.8$.

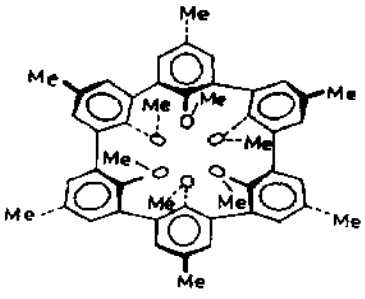
patterns from the two can be observed. Thus, in extractions, polymer **CXXV** displays a high K^+ selectivity with regard to the two-phase systems, whereas it is Rb^+/K^+ selective in the three-phase systems [603]; the latter observa-

tion is the result of an effective containment of K^+ in the non-polar phase and facilitated release of Rb^+ into the receiving aqueous phase. Among the techniques for the study of the polymer macrocycles, spectrophotometry has enjoyed a wider applicability while potentiometry [614], viscosity [616] and ^{13}C as well as ^{23}Na NMR [615] show promising applicability. A new spectrophotometric method involving competition between a soluble ligand and an immobilized crown has been proposed as a versatile tool for evaluating their interaction with M^{z+} [617].

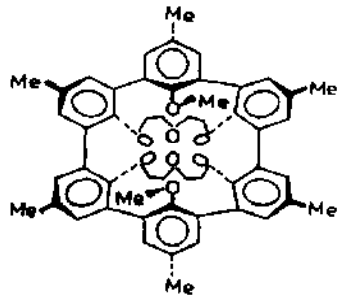
The anion effect on the complexing behaviour of the polymer macrocycles can be detected despite their high complexing ability. The anion effect is observed in the selectivity ratios of different M^{z+} for pic^- versus Cl^- [55], and in stability constants for BPh_4^- vs. pic^- [618,619]. Epoxy polymers carrying diaza crown units, however, show comparable stability constants in spite of a very different ratio of complexation [620]. Other significant developments in the area of polymer macrocycles are the use of polymer membranes [611–613] and of photoresponsive polymer crowns [621–624].

(ix) Category 9: other macrocycles

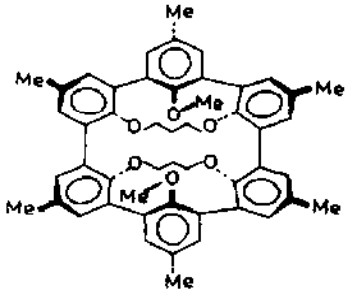
There is a variety of macrocycles which do not conform to categories (i)–(viii). Prominent among them are the so-called cavitands [625], synthesized and investigated exclusively by the Cram group [626–636]. They possess enforced (rigid) cavities while the interior may be spherical, hemispherical, ellipsoidal, oblong, collar or any other designable form. A cavitand such as **CXXVI** [626] (Fig. 49), with a spherical interior is termed a spherand. Such molecules are fully organized during the very synthesis in contrast to other macrocycles which become organized only during complexation [627]. Spherand **CXXVI** has the distinction of being the strongest known binder of Li^+ and Na^+ [628,629]. This and related macrocycles, including **CXXVII** [630] and **CXXVIII**, also display an unusual discrimination in that not only the low charge density K^+, Rb^+ and Cs^+ are rejected but also the high charge density Mg^{2+} and Ca^{2+} [628]. X-ray structural analyses of LiCl(**CXXVI**) [627], $NaCH_2SO_4$(**CXXVI**) [627], $LiFeCl_4$(**CXXVII**) [628] and LiCl(**CXXVIII**) [628] have been carried out. Perhaps because of the bridges present in **CXXVII** and **CXXVIII**, one of the oxygens is non-bonding [628] for each macromolecule (Table 5). Related macrocycles possessing cyclic urea moieties bound to anisyl or methylene units also exhibit high extraction rates and high cation selectivities [631]. Macrocycle **CXXIX** [632] is a typical hemispherand which has a better complexing ability [633] than crowns. Modified hemispherands have also been introduced [636]. NMR work on M(pic) in D_2O-saturated $CDCl_3$ [628] reveals that, cation–cavity size compatibility being present, the complexing ability



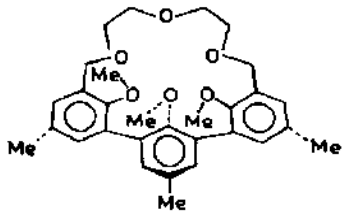
CXXVI



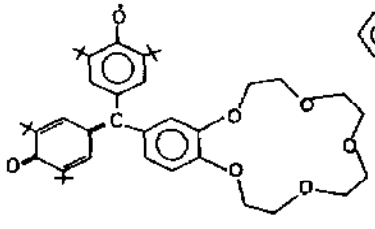
CXXVIII



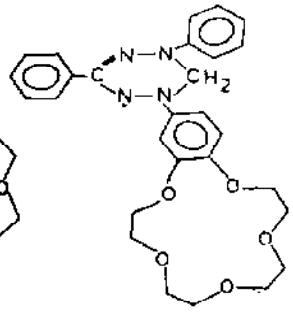
CXXVII



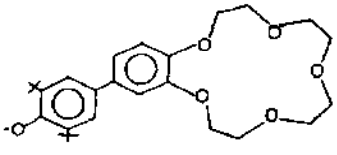
CXXIX



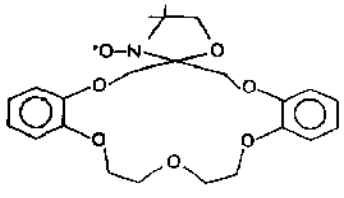
CXXX



CXXXI

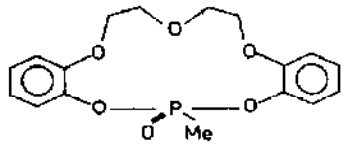


CXXXII

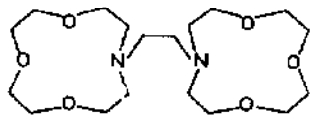


CXXXIII

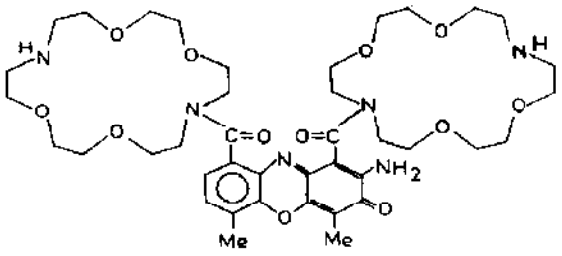
Fig. 49. Category 9 crown-related macrocycles (other macrocycles): **CXXVI–CXXXVII**.



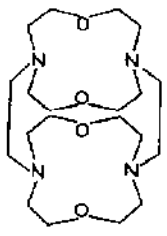
CXXXIV



CXXXVI



CXXXV



CXXXVII

Fig. 49. (continued).

towards Li^+ and Na^+ lies in the order spherands > cryptands > hemispherands > crowns.

The spin-labelled crowns [637–645] designed primarily for study of the diamagnetic M^{z+} through ESR spectroscopy, utilize the availability of an unpaired electron in a suitable moiety attached to the crown ring. This approach is understandably complementary to that employing an anionic radical as the counter-anion [265–267,276]. With Na^+ [639,641], K^+ [639,641] and Rb^+ [641], the galvinoxyl-labelled B15C5, **CXXX**, shows 1 : 1, 1 : 2 and 1 : 2 interaction stoichiometries respectively, which is in accord with the normal interactivity displayed by B15C5. Similar behaviour has been noted for nitroxide-labelled B15C5 [637] towards Na^+ and K^+. Intriguingly, however, there is little effect of the change of anion (NCS^-, Br^- or I^-) for 1 : 1 as well as 1 : 2 stoichiometries [641]. The interaction stoichiometry of **CXXXI** with Na^+ is 1 : 2 and the two verdazyl groups in the complex stack face-to-face with each other [640]. Sandwich complexation is not a normal feature of Na^+ [9]; in this system it appears dictated by the suitably designed **CXXXI**. The unusual complexing ability of **CXXXI** towards K^+ is noted, with which it forms a polymeric structure $(1:1)_n$ [640] with alternating arrays of K^+ and **CXXXI** instead of the expected 1 : 2 sandwich. It is exciting to note that the phenoxyl-labelled B15C5, **CXXXII**, yields two types of 1 : 2 complexes possessing different conformations plus a 1 : 1 complex in equilibrium [642]

for a mixture of Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} in ethanol.

In contrast to **CXXX–CXXXII**, each of which possesses an unpaired electron far away from the donor ring, **CXXXIII** and related macrocycles possess the unpaired electron very much nearer the ring. Their complexing ability is drastically reduced [645] suggesting an adverse contribution from the unpaired electron.

The complexing behaviour of macrocycles containing phosphonyl group(s) such as **CXXXIV** [646] has also been investigated [646–649]. The phosphonyl groups play a dominant role in cation bonding [646]. Such macrocycles resemble those containing carbonyl group(s) but the electronegative phosphorus should reinforce the basicity of the oxygen carried by it; carbon, of course, cannot make such a contribution.

Porphyrins appended with one or more (up to four) B15C5 moieties at the methine position(s) have been synthesized and the complexing behaviour of such natural–synthetic macrocycles has been investigated [650]. As expected, the central part binds transition metal ions such as Co^{2+}, Cu^{2+} and Zn^{2+} while the peripheral crown displays recognition towards M^{z+} (Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+}). The tetrasubstituted B15C5-porphyrin is highly selective for K^+. Complexation of a diaza-crown capped cyclodextrin with M^{z+} has also been investigated [651].

Although bis-crowns have been extensively investigated, similar linking of aza-crowns has been much less studied so these macrocycles are yet to establish their full potential. Macrocycle **CXXXV**, regarded as an analogue of cryptomycins, complexes M^{z+} rather efficiently [652]. Macrocycle **CXXXVI** is interesting in that, despite the presence of one nitrogen in each macrocycle moiety, it causes an intramolecular sandwich encapsulation of even Li^+ [653]. A related macrocycle **CXXXVII** displays a distinct preference for Na^+ in that from a solution containing Li^+, Na^+ and K^+ (as Br^- plus BF_4^-) only a complex of $NaBF_4$ is crystallized. X-ray structural analysis of the complex [654] reveals Na^+ to be 8-coordinated exclusively with the ligand donor atoms and exists charge separated from the anion.

D. DEVELOPMENTS BETWEEN 1984 AND 1986

This section has been consciously separated from the main text not only to single out the latest trends in the work on MCM but also to enable the reader to recognize that the conclusions concerning reaction trends and chemical principles derived earlier permeate through further work.

(i) Crowns

Of all the studies on M^{z+}–crown systems, the single-crystal structural work has been most informative.

(a) Solid state studies

X-ray structural analysis of $LiN(SiMe_3)_2(12C4)$ [655] reveals that the complexed Li^+ remains paired with the counter-anion though, unlike LiNCS(12C4) [161], the Li^+–O bond distances have a greater disparity (2.09–2.39 Å). This system represents the first structural characterization of a mononuclear amide. Lithium prefers pairing even with a weakly counter-acting anion such as NO_3^- as also revealed by structural analysis of $LiNO_3$(MCM), where MCM is B14C4 [656] or the dimethyl derivative of B14C4 [657]. However, for a charge-delocalized anion such as a carbanion, which lacks a formal donor atom ("anionic" site), Li^+ can not only be charge separated from the counter-anion but may also display a coordination number as high as eight; X-ray structural features of $[Li(12C4)_2](PPh_2)$ [658], $[Li(12C4)_2](AsPh_2) \cdot THF$ [658], $[Li(12C4)_2](CHPh_2)$ [659], $[Li(12C4)_2](CPh_3) \cdot THF$ [659], $[Li(12C4)_2][CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)] \cdot Et_2O$ [660] and $[Li(12C4)_2][RPBMes_2] \cdot THF$ (R = Ph, C_6H_{11} or Mes (Mes = 2,4,6-$Me_3C_6H_2$)) [661] have established this feature.

The complex $(Li(pic))_3(DB30C10)_2 \cdot 5H_2O$ [662] is a 3 : 2 complex and represents the first example of this unique stoichiometry for Li^+. Precise bonding modes of the cation are not, however, known as X-ray structural information is not available. The X-ray structural analysis of the complex $(Li(pic))_2(DB36C12) \cdot 2H_2O$ has revealed [662] each Li^+ to be 5-coordinate through just two crown oxygen atoms, the phenoxide and an *o*-nitro oxygen of the counter-anion and a water molecule. The coordination of both the water molecules in this complex, despite the availability of many crown oxygen atoms, further suggests a solventphilic character for this cation as was first highlighted through the structural analysis of $[Li(pic)(H_2O)_2]$B15C5 [188].

With DB18C6, the Na^+ salts of the monoalkyl esters of benzeneazophosphonic acids yield 1 : 1 monohydrated or anhydrous complexes from acetonitrile and/or ethanol [663], but not from methanol (cf. ref. 664). With DB24C8 the results are more interesting in that the same salts consistently yield 1 : 1 complexes from 1 : 1 as well as 2 : 1 reaction mixtures (instead of the expected 2 : 1 bimetallic complexes) [664]. The formation of 1 : 1 complexes provides an additional example of the role of the anion in modifying the interaction stoichiometry (cf. ref. 91). X-ray analysis of $W(PMe_3)_3H_5Na(15C5)$ reveals that the anionphilic Na^+ is displaced by 1.1 Å with respect to the crown ring [665].

X-ray structural analysis of $(NaPF_6)_2(DB36C12)$ [666] has revealed each Na^+ to be 7-coordinate through five crown oxygen atoms and two fluorine "atoms" of the mononegative hexafluorophosphate wherein the cation is displaced by 0.45 Å towards the phosphorus atom from the mean plane of the five oxygen atoms. Coordination of the two fluorine atoms with Na^+ is

significant as neither carries a formal charge. Recent work on the 2:2 complexes, $Na_2(Cu_2Cl_6)(B15C5)_2$ [667] and $Na_2(Cu_2Cl_6)(DB18C6)_2$ [667], further suggests the role of the dinegative nature of the anion as also argued, say, for the complex $K_2(Mo_6O_{19})(18C6)_2 \cdot H_2O$ [186] (Section B (ii) (c)).

X-ray structural analysis of $[K(B15C5)_2]NO_3 \cdot H_2O$ [668] further confirms the genuine feature of K^+ to undergo charge separation [9] in favour of the neutral ligands; charge separation has apparently taken place even for B15C5 with bulky *t*-alkyl substituents [669]. However, this cation may not undergo charge separation in a system such as $K_2(Cu_4I_6)(15C5)_2$ [670] wherein the dinegative anion holds each K^+ through three anionic sites (K^+–I^-, 3.85 Å).

The X-ray structural results of the additional new K^+–crown complexes, $K_7[(Cu_4I_6)(Cu_8I_{13})](12C4)_6$ [670], $K(Cu_3I_4)(DB18C6)$ [670], [K(DB30C10)]NCS · H_2O [671], [K(18C6)](perchlorotriphenylmethide) [672,673], [K(DB18C6)]($Al_2Me_6N_3$) · 1.5(1-methylnaphthalene) [674], [K(DB18C6)](Al_2Me_6OPh) [675], K(μ-H)Mo(*n*-$C_5H_5)_2$(18C6) [676], $W(PMe_3)_3H_5K(18C6)$ [665], $K_2(Cu(S_2C_2O_2)_2)(18C6)_2 \cdot DMF$ [677] and KNO_3(DM18C6) [678] have now become available, where DM18C6 = dimethyl-18-crown-6. Interestingly, the K^+–O distances in [K(DB30C10)] NCS · H_2O [671] are longer than those in anhydrous [K(DB30C10)]NCS [148]. For K(μ-H)Mo(*n*-$C_5H_5)_2$(18C6) [676] and $W(PMe_3)_3H_5K(18C6)$ [665], remarkably, K^+ is pulled out of the crown ring by the anion to the extent of 0.866 Å and 0.76 Å respectively. As mentioned above for $K_2(Cu_4I_6)(15C5)_2$ [670], the dinegative anion in $K_2(Cu(S_2C_2O_2)_2)(18C6)_2 \cdot$ DMF precludes charge separation of K^+ [677].

The M^{z+}–crown stoichiometries reported for 18C6-crowns [679,680] with Na^+ and K^+ in ethereal solvents are rather intriguing. Synthesis of complexes from such solvents is not a common feature of the chemistry of M^{z+}–crown complexes. However, M^{z+}–crown complexes can be synthesized even from chloroform (cf. ref. 685).

Under most conditions, DB24C8 yields bimetallic complexes with Na^+ and K^+ [90]. X-ray analysis of $(Na(onp))_2$(DB24C8) [179] and $(KNCS)_2$(DB24C8) [177,178], synthesized by one of us, has indeed revealed the two cations for each complex to be encapsulated within the cavity of the crown. Since coordination of M^{z+} with a neutral ligand is a function of the counter-anion, we believed that using an appropriate anion it should be possible to control and regulate the Lewis acidity of Na^+ and K^+ to an extent that under some conditions DB24C8 would be able to form a mixed-cation complex of Na^+ and K^+. Indeed we found that for sal^- and pic^- the complexes $NaK(sal)_2(DB24C8)_2$ and $NaK(pic)_2(DB24C8)_2$ could be synthesized. X-ray structure of the former complex revealed [681] that the system is a co-crystallization of the Na_2 complex and K_2 complex (Fig. 50)

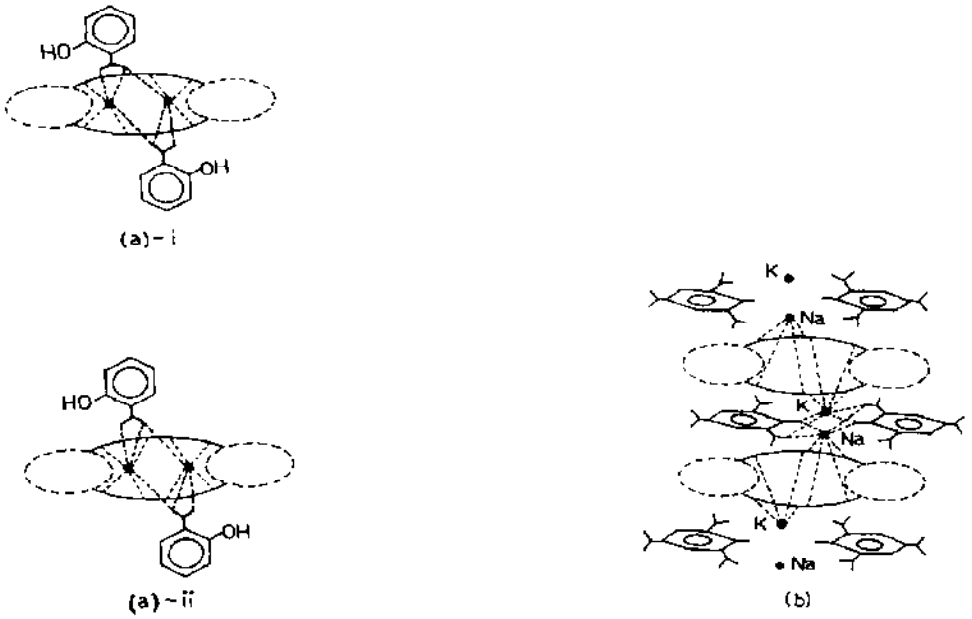


Fig. 50. A schematic view of the mixed cation–bimetallic complexes of Na^+ and K^+ with DB24C8. (a) $NaK(sal)_2(DB24C8)$: (i) $Na_2(sal)_2(DB24C8)$ and (ii) $K_2(sal)_2(DB24C8)$; (b) $NaK(pic)_2(DB24C8)$.

so that a unit cell in the crystal lattice contains two molecules of $[Na(sal)]_2(DB24C8)$ and two of $[K(sal)]_2(DB24C8)$ ($Z = 2 + 2$). The bonding modes of K^+ and Na^+ in the respective molecules are strikingly comparable with regard to sal^- anions but different towards DB24C8. X-ray analysis of $NaK(pic)_2(DB24C8)$ revealed that half of the crown molecule binds K^+ while the other half binds Na^+ from the other axial side so that each cation is within a pseudosandwich of the alternated stacks of two pic^- anions as well as a molecule of DB24C8. A molecule of DB24C8, therefore, indeed picks up one Na^+ and one K^+ when pic^- is the charge neutralizer (paper in preparation).

The X-ray structural results for $[Rb(B15C5)_2]NO_3 \cdot H_2O$ [682], which is isomorphous with $[K(B15C5)_2]NO_3 \cdot H_2O$ [668], provide additional proof of Rb^+ mimicking the chemistry of K^+ as concluded earlier [175]. The complex $Cs_2(Al_3Me_9SO_4)(18C6)$ [683] constitutes a unique example of a 2 : 1 complex of the large Cs^+ with the smaller 18C6; each Cs^+ is 9-coordinate through interaction with six crown oxygen atoms, two sulphate oxygen atoms and the other Cs^+ cation which establishes a so-called metal–metal bond.

The M^{2+}–crown complexes examined crystallographically within these three years are $Ba(pic)_2(B15C5) \cdot H_2O$ [121], $[Ba(dnb)_2(B15C5)]_2$ [115] (Fig.

16), $Sr(NO_3)_2$(DC18C6 *cis–syn–cis*) [684], $M(NO_3)_2$(DM18C6) (M^{z+} = Ca^{2+}, Sr^{2+} and Ba^{2+}) [685], $Ca(NO_3)_2$(TM18C6) [685], where TM18C6 = tetramethyl-18-crown-6. A detailed structural report [686] on $Ba(NCS)_2$-(DC18C6 *cis–syn–cis*) · H_2O [106] has also appeared. Calcium in [$Ca(dnb)_2$-(B15C5)](B15C5,3H_2O) [114] is effectively chelated through the carboxylate moiety of either dnb^- whereas each of Na^+ and Ba^{2+} for the same anion in Na(dnb)(B15C5) · H_2O [169] and [$Ba(dnb)_2$(B15C5)]$_2$ [115] involves only a monodentate interaction. Obviously, therefore, a pronounced and profound anionphilicity of Ca^{2+} occurs.The results for the DM18C6 complexes [685] suggest that for an O donor (crown) the discrimination for the trio Ca^{2+}, Sr^{2+} and Ba^{2+} is not marked within the group.

Newer approaches towards the solid state examination of M^{z+}–MCM systems include differential scanning calorimetry (DSC) [687,688] and solid state ^{13}C NMR [689,690]. The phase diagram of the system KNCS–DB18C6 has been investigated through DSC and so also has the enthalpy of formation of the complex in different states [687]. A 1 : 1 complex is formed, congruently melting at 245 °C; it is not miscible with the components in the solid phase. The complex is, however, miscible with the crown (but not with KNCS) in the liquid phase, suggesting the formation of a 1 : 2 complex. DSC has also been used to study the thermal stability of KX–DB18C6 (X = NCS, Br, I, NO_3) systems [688]. The solid state ^{13}C NMR spectra of DC18C6 isomers in the presence of NaBr, KI, CsNCS and KI_3 or $Ba(NCS)_2$ have been obtained by cross polarization–magic angle spinning (CP–MAS) [689]. This has been claimed to be an advantageous technique in that it can enable examination of conformation in solution vis-a-vis in the solid.

(b) Solution studies

A recent review by Izatt et al. provides extensive thermodynamic and kinetic data for cation–MCM interaction through early 1984 [691].

Interest in the determination of the equilibrium constants for diverse M^{z+}–crown systems using different techniques has, of course, continued [692–712]. The spectrophotometric determination of equilibrium constants for Na^+–crown and K^+–crown complexes in dioxane has revealed [695] interesting anion dependence of the stability for each cation. This gives weight to our suggestion (ref. 9; Table 3, footnote c) that the stability values under a given set of conditions are a function of the charge neutralizing anion and that the anion should also be specified when describing the stability results. With ans^-, strikingly, the order of complexing abilities for Na^+ is 18C6 > DC18C6 > MB18C6 > TBDB18C6 > DB18C6 while with pic^- the order is practically reversed (DMDB18C6 > TBDB18C6 > DB18C6 > DC18C6 > 18C6). No such reversal in the order is observed for K^+. This disparity in the behaviour of Na^+ and K^+ should primarily be because Na^+

is distinctly more anionphilic [9] than K^+—an effect which is displayed because of the poor solvating ability of dioxane. Intriguingly, however, no anion dependence is observed for the stability values of Na^+–18C6 systems through ^{23}Na NMR measurements although anion dependence in water and methanol is vividly brought out for the systems through potentiometric investigations [699].

As expected, the log K values decrease, in general, in the order unsubstituted, monobenzo- and dibenzo-substituted MCM, and interestingly, the decrease in this order is more pronounced for M^{2+} than for M^+ [700]. This conclusion results from work on M^{z+}–B15C5, M^{z+}–B18C6, M^{z+}–DB18C6, M^{z+}–DB21C7, M^{z+}–DB24C8 and M^{z+}–DB27C9 in methanol [700]. Other studies include those on M^+–B15C5, M^+–B21C7 and M^+–B30C10 in 99% DMSO [692], M^+–B18C6 in various non-aqueous solvents [694,696], M^+–DB24C8 in MeCN [697], M^+-substituted DB18C6 crowns in MeCN [698], Li^+–DB14C4 in diverse solvents [693], Cs^+–DB24C8 and Cs^+–DB27C9 in mixed solvents [701], Cs^+–DB21C7 and Cs^+–DB24C8 in mixed solvents [702], M^{z+}–15C5, M^{z+}–C15C5, M^{z+}–B15C5, M^{z+}–18C6, M^{z+}–DC18C6 and M^{z+}–DC24C8 in methanol [703], Ba^{2+}–12C4 [704] and Ba^{2+}–18C6 [704,705] in methanol and Na^+–B15C5, K^+–B15C5 and Na^+–DB30C10 and K^+–DB30C10 in MeCN–H_2O [705a].

The multinuclear NMR studies of M^+–crown complexation, employing molten salts at room temperature, display a different pattern with respect to the general trend of equilibrium constant studies [713]. Multinuclear [714] and ^{13}C NMR [715] relaxation studies on M^{z+}–crown systems and ^{23}Na NMR spectral studies in methylamine as a function of temperature [716] have also been performed.

A new advance is the development of an NMR method for the determination of formation constants invoking the competition of two cations for a given ligand [708,709]. This competitive NMR technique has been claimed to be advantageous in that it enables (i) investigation of those cation–MCM systems for which the nuclear properties of the cation are not favoured towards NMR measurements and (ii) investigation of systems possessing such formation constants which are too large to be measured by the conventional NMR technique involving a single cation. The use of electrohydrodynamic mass spectrometry (EHMS) [710] for the evaluation of relative stability constants of M^{z+}–18C6 systems (in glycerol) is worth highlighting. The feature of the technique is that it does not incorporate particle bombardment.

A microcomputer-controlled polarographic system has been developed for the determination of the stability constants of M^+–crown complexes [711]; the computerized method compares favourably with the manual method. The stability constants of Sr^{2+}–18C6, Ba^{2+}–18C6 and even Ra^{2+}–18C6 in

an aqueous solution have been determined by d.c. and radio polarography [712].

Viscosity coefficients of M^+–18C6 complexes have been determined for Cl^- as the counter-anion [717]. The temperature dependence of the Walden product of the K^+–18C6 complex in water has been investigated [718].

Inoue and Hakushi have generalized [719] for a wide range of thermodynamic data that (i) the stabilities of M^{z+}–MCM systems are related to the entropy–enthalpy compensation effect and that (ii) the M^{z+}–MCM interaction can be simulated from the slopes and intercepts of ΔH vs. $T\Delta S$ plots which are fairly linear.

With regard to the solution structures of the crown complexes, a ^{23}Na NMR study of $NaBPh_4$–DB30C10 aggregation in nitromethane has been reported and a model based on the coexistence of 1 : 1, 2 : 1 and 3 : 2 complexes has been proposed [720]. The characteristic ^{23}Na relaxation rates and chemical shifts of the aggregated complexes are in accordance with a structure of $Na^+BPh_4^-$ ion pairs in a state of interaction with DB30C10. The researchers noted a degree of aggregation [721] for $NaBPh_4$–DB24C8 in the same solvent.

With the small (and rather hydrophilic) 12C4, Mg^{2+} can also form a 1 : 2 sandwich in solution provided the cation is not strongly solvated (as in CD_3NO_2) [722]. The 1 : 1 complexation of the anionphilic Ca^{2+} with 15C5 crowns (15C5, B15C5 and C15C5) is established further whereas each of Na^+, K^+, Rb^+, Cs^+, Sr^{2+} and Ba^{2+} forms 1 : 1 as well as 1 : 2 complexes with the same MCM [703]. For 18C6 or DC18C6, only Cs^+ forms a 1 : 2 complex [703]. Circular dichroism has been used to study the state of ion pairing for KNO_3–DM18C6 in solution and the results correlated with the X-ray structural results for the solid state [678].

The effect of the alkyl group substituted on the ring appears to be illustrated through work on the synthesis of M^{z+} complexes with DM18C6 and TM18C6 using a solvent of highly reduced polarity (chloroform) in which the M^{z+} salts (nitrates) are expected to be strongly paired. The results of the synthesis studies reveal [685] TM18C6 to be relatively weaker in that it fails to yield complexes of the larger cations (K^+, Rb^+, Sr^{2+} and Ba^{2+}) compared with DM18C6, for which M^{z+} $(NO_3)_z^-$–DM18C6 complexes crystallize. The effect does not appear to be steric in nature as DM18C6 yields complexes also of the above-mentioned larger cations. This observation leads to the rather uncommon conclusion that the methyl substituents are perhaps exercising a $-I$ effect (cf. ref. 722a); the negative effect of the methyl substituents on the crown ring is also apparent from the stability data of the polymethyl crowns vis-a-vis those for the analogous non-methylated crowns [722b].

The kinetics of cation–crown complexation have been studied by ^{23}Na

NMR [723–725], ^{133}Cs NMR [726] and ultrasonic [727–730] techniques. The ^{23}Na NMR studies [723] have revealed that, for complexation with 18C6, exchange of Na^+ between the free and the complexed sites is slow at room temperature and the predominant exchange mechanism is dissociative when BPh_4^- is the counter-anion. With NCS^- as anion, the Na^+ exchange is fast at room temperature and the mechanism is predominantly bimolecular.

^{23}Na NMR kinetic studies (for Na^+–18C6) have revealed [725] the complexation–decomplexation mechanism to be dependent on the nature of the solvent. This observation corroborates the earlier postulate [246,727] relating to the role of solvent in modifying the number of observable steps.

The D NMR studies of the kinetics of Mg^{2+}–15C5 vis-a-vis the Mg^{2+} system have revealed [731] that solvation (with DMF) is highly favoured for the crown-complexed cation. We are using this observation to explore the facilitated solvation of Grignard's reagent with feebly polar solvents such as THF and ether (work in progress).

A variation in the lipophilization technique has been made [732] through the use of solvent-swollen microporous polystyrene resin to which a crown (or any multidentate) is anchored. The immobilized ligand N* can be made to compete with a suitable ligand S for a salt leading to an exchange of N* with S. This technique enables evaluation of the relative ligand affinities of different multidentate ligands towards a cation as demonstrated for various crowns, using Li(pic) and Na(pic) in toluene [732]. Lipophilization studies are gaining additional importance [695]. Synergistic effects of the additives on the complexation of DB18C6 with Na(pic) and Na(ans) in toluene [733] have been investigated. Although chloroform carries a rather feebly polarized hydrogen, synthesis of $M(NO_3)_2$–DM18C6 complexes [685] through reaction of the metal nitrates with the crown in this solvent is very much a synthesis of complexes through lipophilization.

Solubilization of potassium ethylenediamine tetraacetatocobaltate(III) by several crowns in MeCN has been studied spectrophotometrically [734]; the solubility enhancement was found to be dependent primarily on the magnitude of the association constant of K^+ with the crown concerned. However, such a solubilization phenomenon is distinct from lipophilization because a solvent such as MeCN is polar enough to cause a degree of solubilization by virtue of its solvating ability.

The extraction studies of M^{z+}–crown systems are attracting increasing attention [62,735–755]. A phenomena-oriented account of the earlier literature has been published [62]. Further insight into the effect of solvent (diluent) [735] and of the counter-anion [736] has been obtained using a variety of crowns. Control on M^{z+} extraction through adjustment of the methylene chain length has been exercised. Extraction with the less symmetrical crowns has been found to be, in general, less effective than with the

symmetric crowns [739]. The mechanism of transfer of Na^+ across the water–nitrobenzene interface, as facilitated by DB18C6, has been investigated using the a.c. polarographic method [750]. The site of complex formation is the interface.

A comparative study of the different extraction systems for spectrophotometric determination of K^+ with 18C6 has been made [740]. Taking advantage of the fact that 12C4 complexes Na^+ selectively in the presence of other M^+, a method for determining serum Na^+ concentration has been developed [742]. Factors determining the selectivity for membrane electrodes based on N15C5 by liquid–liquid extraction have been evaluated [744]. The crown DC18C6 has been claimed to separate Rb^+ from most M^{z+} [746]; tolerance levels for K^+, NH_4^+ and Ba^{2+} have been found to be low. The solvent extraction of Na^+ with various crowns has also been investigated [747].

Cation transport across a chloroform bulk membrane using binary Tl^+–M^{z+} [756], K^+–M^{z+} [756], Cd^{2+}–M^{z+} [757] and Hg^{2+}–M^{z+} [758] mixtures has been investigated for a series of MCM carriers. Facilitated transport from ternary cation mixtures [759] has also been investigated. The parameters which affect cation transport, such as membrane configuration, cation–MCM complex stability, partitioning of MCM between membrane and aqueous phases, MCM concentration, anion type, ion concentration, membrane solvent type and receiving phase composition have been discussed in detail [760]. The conditions necessary for designing cation selectivity in liquid membrane transport have also been discussed [761].

The relationship between the extractability and the rate of transfer of K^+ by macrocyclic carriers including crowns has been investigated in chloroform membrane systems [762]; the rates of ion uptake, ion release and ion transport and the liquid–liquid extraction constants have been determined. In continuation of the earlier observation [362] that the overall rate of cation transport is "occasionally" governed by the rate of release rather than by the rate of uptake, it has now been observed that [762] the rate of uptake governed the overall rate of transport through the liquid membrane for the MCM employed in the study (18C6, DB18C6, DC18C6 and polynactin). In another study it was observed that [763] the rate of transport is controlled by the rate of uptake in the region of low stability constant and by the rate of release in the region of high stability constant.

The transport ability of some common ionophores including 18C6 across dichloromethane has been noted to improve with a decrease in temperature [764]. The influence of stirring rate on the transport of cations across unsupported liquid membranes has been examined for several systems [765]. The KNO_3–DB18C6 combination was chosen as a representative system involving an unionized MCM for the study of diffusion rate-limited trans-

port. Such systems showed continuous variation of transport rate over the range 100–600 rev min^{-1} in stirring speed. Other studies include electrodialysis involving bulk liquid membrane (1,1,2,2-tetrachloroethane) with DB18C6 as a carrier [766], and transport studies of an anion ($AgBr_2^-$) across an emulsion liquid membrane using M^{z+}–DC18C6 types of species as counter-cations [767]; the quantity of $AgBr_2^-$ transported depends on the counter-cations and decreases in the order $K^+ > Na^+ > Li^+ > Mg^{2+}$, in accordance with the decrease in the stability values for the M^{z+}–DC18C6 species.

Substitution of an alkyl or phenyl group on a crown increases its lipophilicity and regulates also the basicity of its oxygens; the former feature is more closely linked with the ultimate solubility characteristics of the cation–crown complex whereas the latter is more fundamental to the stability data. Since the methyl group can [722a] also exercise a $-I$ effect (see the sub-section on solution structures; vide supra), the role of methyl and phenyl as substituents could be comparable [768]; increased lipophilicity as a consequence of these substitutions could also make the ionophore increasingly acceptable to the non-polar phase thereby leading to a reduction in transport. However, a consistent increase in Li^+ transport for the two substituents [768] is really intriguing because as many as three factors, viz. electronic factor, lipophilicity and steric effect, are involved.

(c) Theoretical studies

The thermodynamic data on M^+–crown systems have been derived through CNDO/2 calculations [769]. Ab initio quantum chemical calculations have revealed that the most stable conformation of 12C4 (viz. maxidentate) is maintained in its complexes with Li^+ and Na^+ [770] as well as with Mg^{2+} and Ca^{2+} [771]. The most stable conformation for the corresponding tetraaza analogue is, however, the alternate [770,771].

(ii) Crown-related macrocycles

Category 1 MCM. The complexation of crown-4 derivatives of 13- through 16-membered rings, each carrying a long aliphatic chain, has been investigated [772]. Some lipophilic 14-crown-4 derivatives display remarkably high selectivity for Li^+ over Na^+ [772]. Accordingly, Li^+-selective polymeric membrane electrodes based on dodecylmethyl-14-crown-4 have been devised [773]. The extraction of Li^+ (as pic^-) from water into dichloromethane using didecalino-14-crown-4 has been investigated [774]. A high K^+/Na^+ selectivity of tridecalino-18-crown-6 has been witnessed through extraction as well as potentiometric titration studies [775]. Using tridecalino-18-crown-6 [776], extraction of K^+ (vis-a-vis Tl^+) from water into chloroform has been

investigated, in order to see the embedding effect of decalin walls. Carrier efficiencies and ion selectivities of some oligo-benzo-condensed 18C6 macrocycles have been determined for M^{z+} in liquid membrane electrodes of different composition [777].

The absorption maxima of an azulene crown have been noted to shift hypsochromically on the addition of M^{2+} salts (Ca^{2+}, $\lambda_{max} = 610$ nm; Ba^{2+}, $\lambda_{max} = 612$ nm) [778]. Because of the absence of a heteroatom in the chromophore moiety, the salt-dependent effects have been rationalized in terms of a direct interaction of the complexed cations with the π-system (presumably via the negative polarized five-membered ring) [778]. A fluorescent probe investigation on the effect of M^+ on the micellar properties of a crown ether surfactant has revealed a correlation between the binding efficiency of M^+ and the fluorescence parameters [779].

The X-ray structural analysis of the NaNCS complex of a macrocycle, incorporating propeller substituents, has revealed Na^+ to be within the pentagonal arrangement of five oxygen atoms while NCS^- occupies the pyramidal position [780]; the conformation of the propeller, unlike that of the crown ring, remains unaltered. The X-ray structural analysis of KNCS(**CXXXVIII**) reveals [781] that the cation is coordinated with all the six oxygen atoms of the MCM while maintaining ion pairing with the counter-anion. With regard to the electronic aspect, **CXXXVIII** (Fig. 51) is not much different from 18C6 and expectedly, therefore, the structural aspect of the KNCS complexes of the two is fairly comparable.

Category 2 MCM. Among these macrocycles, the status of the "lariat ethers" has been further consolidated [715,782–791]. The first X-ray structural analysis of a lariat ether complex (with NaBr) has been carried out wherein an ester carbonyl group of the lariat moiety has been found to interact directly with the ring-bound cation [782]; it has also been established that an ester carbonyl is a better donor than an ether oxygen. The ^{13}C NMR relaxation times have been determined for several lariat ethers, in the absence and presence of Na^+, K^+ and Ca^{2+} [715]. The stability constants (and enthalpies as well as entropies) for interaction of Na^+, K^+, Cs^+ and Ca^{2+} with lariat ethers have been determined [783]; generally, little effect on the stability value is noted either by lengthening the pendant arm (and by incorporating an additional donor site) on the 18-crown-6 compounds or by appending the pendant arms having oxygen atoms on the C-pivot atom of the 15-crown-5 compounds. Similarly, it has been independently found [784] that despite the presence of ether oxygen atoms in the side-chain, the complexing ability of the alkyl lariat ethers towards Na^+ and K^+ does not differ significantly from that of the corresponding alkyl crowns. The effect of the position of the electron-donating side-arm of 16-crown-5 towards the

complexing ability for Na^+ and K^+ has also been investigated [785]. Using double-armed 16-crown-5, a marked and a specific enhancement in the cation-binding abilities has been observed through extraction studies [786].

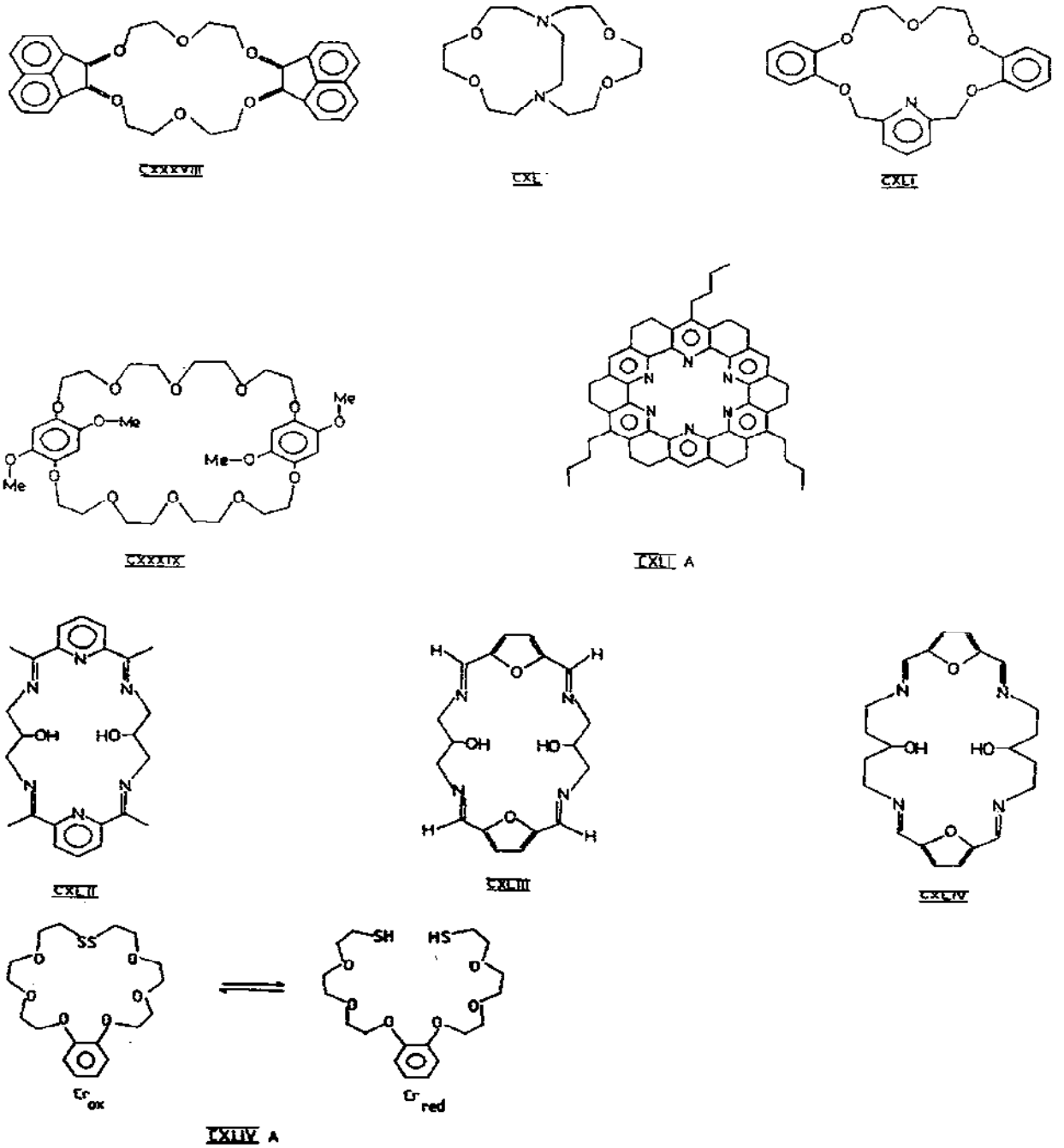
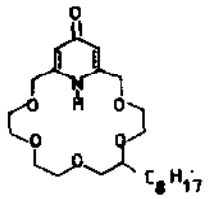
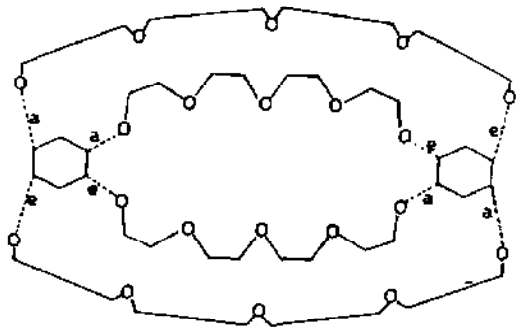


Fig. 51. Newly studied crown-related macrocycles: **CXXXVIII–CXLV.**



CXLIV B



CXLV

Fig. 51. (continued).

The complexation of Na^+ and K^+ with some C-pivot lariat ethers using ion-selective electrodes has been investigated [787].

Cyclic voltammetric studies on lariat ethers in the presence and absence of Li^+, Na^+ and K^+ have revealed [788] both cation-binding enhancements [791] and the cation-binding selectivity for such electrochemically switched MCM (accomplished by one- and two-electron reductions of a quinone side-arm). The variety of the lariat ethers has been increased by introducing epoxy [789] and chromogenic [790] lariat ethers. Extraction studies have revealed [792] that, of the various novel (benzyloxy)methyl-substituted macrocycles, the strongest Li^+ complexation is observed with [(benzyloxy)methyl]14-crown-4.

To evaluate the binding characteristics towards M^{z+}, a method involving surface potential measurements has been developed for macrocycles such as octadecyloxymethyl-18-crown-6 [793].

Category 3 MCM. **CXXXIX** forms a 2 : 1 bimetallic complex with NaNCS, viz. $[(NaNCS)(Na^+)(\mathbf{CXXXIX})(H_2O)](NCS^-,H_2O)$ [794]; X-ray structural analysis of this complex has revealed that $Na^+(1)$ is 6-coordinate and ion paired with NCS^- while $Na^+(2)$ is 8-coordinate through seven MCM oxygen atoms and a water oxygen atom. The non-coordinated NCS^- is hydrogen bonded with the non-coordinated water molecule which, in turn, is hydrogen bonded with the cation-coordinated water molecule. This complex represents a unique system wherein two halves of a symmetric molecule interact differently with two metal ions. Obviously, it is the steric and conformation aspect rather than the electronic effect which can be linked with the difference in M^{z+}–ligand interaction through the two halves. Apparently, one cation at first undergoes complexation with one half of the MCM. As a consequence of this, the conformation of the second half is modified to

behave differently with the second cation. The X-ray structural analysis of a 1 : 1 complex of KNCS with an MCM containing a 1,1′-binaphthyl moiety and two phosphonate groups reveals K^+ to be charge separated from NCS^- [795]. The sodium perchlorate complex of an MCM incorporating a 15C5 moiety and *vic*-dioxime groups has been synthesized [796]; the X-ray analysis would be interesting.

Substituent effects on extraction and transport behaviour of a series of 4′-substituted B15C5 derivatives have evoked further interest [797]. 4′-Aminobenzo-15-crown-5, for example, has been noted to transport K^+ across dichloromethane 14 times faster than 4′-nitrobenzo-15-crown-5. Thermocontrol of ion permeation through ternary composite membranes composed of polymer–liquid crystal–fluorocarbon MCM has been achieved [798].

There is significant interest in extraction and transport through photoresponsive MCM [64] and further studies have been made on photoresponsive [799–803] and redox-switched [804,805] macrocycles. Particularly interesting are the new [799–801] photoresponsive MCM, each of which carries an ammonium group tail; the ion-binding ability changes in response to an on–off switching. These MCM are so designed that the crown ring can bind the intramolecular ammonium group only on photoisomerization to the cis form. This aspect is shown to be vital towards their extraction efficiency for M^+tos^-. Complexation of new photoresponsive MCM with a fluorescent stilbene cap [802] and an intra-annular 4-methoxyphenylazo substituent [803] has also been studied.

The importance of chromogenic macrocycles is gradually drawing attention [63] but the field is still in an early stage of development. A chromogenic macrocycle, 2″,4″-dinitro-6″-trifluoromethylphenyl-4′-aminobenzo-14-crown-4 has been employed for the spectrophotometric determination of Li^+ [806]. The complexation of azobenzo macrocycles with MI and MI_2 in MeCN has been studied spectrophotometrically and it appears that the azo group is not a particularly favourable component for binding M^{z+} [807]. Other studies include those on Li^+-selective fluorescent emission with crowned benzo- and naphtho-thiazolylphenols [808].

Category 4 MCM. In contrast to the general pattern noted so far that more attention has been placed on intermolecularly bridged MCM than on the intramolecular ones, more attention is now focused on the intramolecular MCM. The potentiometric determination of stability constants (in methanol) of M^+ complexes with a series of diastereoisomeric intramolecularly bridged bicyclic macrocycles using ion-selective electrodes has revealed [809] greater differences in the values than those found for the macrocyclic DC18C6 isomers. Certain new intramolecularly bridged bicyclic multidentates have

been found to complex Na^+ and K^+ in methanol in accordance with the relative size of the cavity with respect to the cation [810]. The X-ray structural analysis of the $Ba(NCS)_2$ complex of a novel intramolecularly bridged macrocycle possessing a total of nine ethereal oxygen atoms has revealed Ba^{2+} to be ion paired with both the NCS^- ions; a coordination number of 11 for Ba^{2+} is a rare feature for the chemistry of this cation [811]. The preliminary results on some intermolecularly bridged crowns [447] have been reported in greater detail [812]. A novel intermolecularly bridged bis-crown with an ammonium tail exhibits transport selectivity for Na^+ over K^+ at lower pH; however, at higher pH, the transport rates for the two ions are comparable [813].

Category 5 MCM. Macrocycle **LVII** (diaza-18-crown-6) has been shown to discriminate between Na^+ (no complexation) and K^+ (1 : 1 complexation) for dnp^- as counter-anion [814]. High resolution ^{13}C NMR spectra of **LVII** have been obtained in the solid state as well as in solution in the presence of NaNCS and KNCS [689]; the solid state spectra of free **LVII** could not, however, be obtained. The macrocycle **LXI** (*N*-phenyl-aza-15-crown-5) interacts weakly with Ba^{2+} in methanol while it is practically "non-interacting" with other M^{z+} [703]. Solution studies of the related MCM [705,815] and liquid membrane transport studies [758,760] have been carried out.

A new chromoionophore, with an azulene unit grafted on the nitrogen atom of an aza-crown, shows a high sensitivity and colour selectivity for Ba^{2+} [778,816]. This colour selectivity can be followed visually through a colour change from yellowish orange to bluish violet; relatively small alterations of colour from orange to red are noticed for other salts including K^+ and Ca^{2+}.

A new bicyclic multidentate, **CXL**, possessing two nitrogen atoms and four oxygen atoms [817] can be treated as a modification of **LVII** wherein a $-CH_2-CH_2-$ link is inserted across the two nitrogen atoms leading to the formation of two cavities, each contracted in size. In contrast to **LVII**, this molecule is remarkably Na^+ selective [817]; the X-ray structural analysis of its LiNCS(hemihydrate) [817,818], NaNCS [817,819] and KNCS [817,819] complexes has revealed that Li^+ is charge separated from NCS^- and is 6-coordinate while Na^+ and K^+ are ion paired and each 7-coordinate.

N-pivot lariat ethers derived from **LVII** can show a $Ca^{2+}/Na^+(K^+)$ selectivity [820]; Ca^{2+} plays a strong organizing role towards the ligand structure [715]. The complexing ability of some 12-membered ring N-pivot lariat ethers has been investigated [821] and this study has been extended to lariat ethers of varying ring sizes (12-, 15- and 18-membered rings); it has been found that the strongest binding for Na^+ occurs when six oxygen atoms are present in the lariat ether, regardless of ring size [822]. Cyclic

voltammetry has been used to study cation complexation by electrochemically switched lariat ethers [788,823]. The X-ray structural analysis of the NaNCS complex of **CXLI**, an analogue of **LXXXIV**, reveals [824] that the cation is 7-coordinate through all the six heteroatoms of the MCM plus the anion from the N-end. The X-ray structural results of several other Na^+ and K^+ complexes of lariat ethers and BiBLE (bibrachial lariat ethers) have been analysed [825,826]; it has been contended that [826] neither the "hole size" nor the "cavity size" concept provides a satisfactory explanation. Furthermore, direct ESR evidence for Na^+-selective, intramolecular ion pairing in redox-switched N-pivot lariat ethers has been presented [827]. A variety of lipophilic polyamine (and polyamide) macrocycles have exhibited excellent cation-transporting abilities for the amino-acid ester salts [828].

Incorporation of the heterocyclic nuclei in the arms of an MCM is a novel variation. A double-armed macrocycle, derived from **LVII** and carrying a furan ring in each arm, displays K^+/M^+ and Ba^{2+}/M^{2+} type of transport selectivities [829,830]. A multi-armed cyclam possessing furan nuclei in the arms is capable of discriminating NH_4^+ from K^+ (and related cations) with regard to transport across a chloroform bulk membrane in the presence of ClO_4^- [831]. A macrocycle derived from **LVII** (possessing *o*-pyridylmethyl groups instead of hydrogen atoms) shows M^{2+} complexation in the order $Ba^{2+} \sim Sr^{2+} > Ca^{2+}$; the preference of this MCM for Pb^{2+} is, however, much higher so that the Pb^{2+}/Ca^{2+} selectivity is of the order of 8.1 [832].

A novel tetraaza macrocycle reveals a noticeable change in its electronic spectrum especially upon contact with an Li^+ salt, indicating its Li^+-selective binding ability [833]. A hydrated $Ba(NCS)_2$ complex of an armed-Schiff-base macrocycle, exclusively an N-donor, has been synthesized [834]. The tetraaza-porphyrinogen substituted by dimethylamino groups shows greater complexing ability than the corresponding unsubstituted MCM [835].

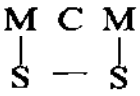
The stability constant of the K^+ complex of a pyridine-fused hexaaza [18] annulene is an order of magnitude higher than that with 18C6 [836] indicating a significant contribution of the pyridine nitrogens in stabilizing K^+. Fusion of six-membered rings on all positions at the periphery of hexaaza [18] annulene affords rigid toroidal macrocycles, termed "torands" by Bell (**CXLI A**, for example); these MCM are shown to possess substantial Ca^{2+}-sequestering ability [837].

The complexation of nicotinic acid crowns has been studied mainly with Mg^{2+} [838]. It has been shown that the oxazoline moiety does not coordinate with Mg^{2+} whereas it prefers K^+. The X-ray structural analysis of the Li(pic) complex of an MCM incorporating furan oxygen atoms reveals that the cation is bound with MCM as well as with the anion [839].

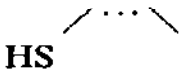
Fenton and coworkers [840] have recently synthesized $Ba(ClO_4)_2$ com-

plexes of **CXLII–CXLIV**, the X-ray analysis of which has been carried out by Bailey et al. The X-ray structural analysis of [Ba(**CXLII**)$(H_2O)_2$]$(ClO_4)_2$ reveals that Ba^{2+} is 10-coordinate through two secondary endogenous alcoholic groups, two pyridyl and four imino nitrogen atoms and two water molecules; neither of the two ClO_4^- anions binds the cation. The complex of $Ba(ClO_4)_2$ with **CXLIII**, viz. $Ba(ClO_4)_2$(**CXLIII**), is anhydrous and anion paired. X-ray structural analysis reveals that Ba^{2+} is 12-coordinate through two secondary endogenous alcoholic groups, two furanyl oxygen atoms, four imino nitrogen atoms and four anionic oxygen atoms provided by the two ClO_4^- anions (each acting bidentate) from different axial sides. The complex $Ba(ClO_4)_2$(**CXLIV**) · EtOH displays incomplete coordination of the cation by the MCM which appears assisted by the increased length of the two bridges joining the secondary hydroxyl groups with the respective imino nitrogen atoms; Ba^{2+} is 10-coordinate through two endogenous secondary alcoholic groups, one furanyl oxygen atom, two imino nitrogen atoms, one ethanol oxygen and four anionic oxygen atoms from the two bidentate ClO_4^- anions from opposite axial sides.

A new method to control the membrane transport efficiency for a macrocycle, **CXLIV A**, containing a disulphide bond in the ring (Cr_{ox}) has been achieved through a redox-switch technique [841]. The



(abbreviated Cr_{ox}) linkage reduced to a



(abbreviated Cr_{red}) type of structure and the transporting ability is drastically changed. Thus, Cr_{ox} transports Cs^+ 6.2 times faster than Cr_{red} across a chloroform membrane [841]. Novel phosphino-aza macrocycles are interesting in that they can bind transition metal ions at phosphorus and M^+ at the aza-crown moiety [842].

Category 6 MCM. Synthetic 32-membered macrocycles possessing ester and ether functions have been examined as models of nactin ionophores with respect to extraction and transport behaviour [843]. Although such MCM are able to extract and transport M^+, no complexation or transport selectivity is observed except for a slight preference for Li^+. MCM bearing reducible quinonoid functions are novel, and in the reduced state display a much stronger preference for Li^+, not observed with a simple quinone [844]. For pic^- as the counter-anion, some macrocyclic dilactones exhibit Ca^{2+}

selectivity with respect to extraction from water into chloroform [845]. In methanol, the stability constants for several macrocycles (including **XCIII**, Fig. 45) incorporating a pyridine nucleus and oxo functions, towards M^{z+}, have been found to be lower than those for the corresponding crowns and the decrease has been attributed to a decrease in the reaction enthalpies [846]. The transport behaviour of such MCM is also distinctly different from that of the unsubstituted MCM [758,760]. The X-ray structural analysis of the KNCS complex of a macrocycle incorporating diester functions and a proton-ionizable triazole subcyclic unit, reveals that K^+–O distances range from 2.862 to 3.061 Å [847].

The macrocycles possessing amide group(s) continue to be interesting [815,848–854]. A bridged bicyclic compound, which differs from MCM of category **4** in that the amide functions are incorporated into the rings, is more selective than its corresponding monocyclic analogue for Ca^{2+} [848]; Ca^{2+}/Mg^{2+} selectivity, too, is enhanced significantly. Using such MCM, Ca^{2+}-selective polymeric membrane electrodes have been devised [849]. The effect of changes in hydrodynamic conditions on the response of the Ca^{2+}-selective membrane electrodes based on amide macrocycles has been studied [850]. The Ca^{2+} selectivity appears to arise from an optimum amide–ether balance in such compounds; MCM containing exclusively the cyclic urea binding sites are poor complexers as well as poor discriminators [851].

For M^+ (as pic^-) in $CDCl_3$, the free energies of interaction of an MCM, which is a "transacylase mimic" incorporating complementary binding and catalytic sites, have been reported [852]; the binding system is composed of three cyclic urea units in a tripod arrangement (which are made rigid through their incorporation into a macrocycle), along with two anisyl, and one *m*-xylyl spacer units [852]. The stability of a dilactam MCM towards M^{z+} is reduced by a factor of more than 10^6 over the unsubstituted MCM, the decrease being mainly [815] due to a decrease in the reaction enthalpies. The ion selectivity exhibited by 20- to 60-membered oligolactam macrocycles (in poly(vinyl chloride) membranes) and its relation to ring size and the substituents of the amide nitrogen atoms, have been examined in detail [854].

Category 7 MCM. A guiding concept for the structure/selectivity relationships in the liquid–liquid extraction of M^{z+} by anionic MCM has been presented [855]. As before, the carboxylic MCM continue to be the most highly investigated among the anionic MCM [856–864]. These MCM are capable of active transport of M^{z+} through the coupled countertransport of protons [865]. Fyles and coworkers have made a detailed examination of the role of such MCM (lipophilic crown ether carboxylic acids resembling

CVIII, Fig. 47) with respect to transport [765,856,857] and complexation [858]. The complexation of such MCM has been studied by potentiometric titrations and by IR as well as NMR spectroscopy; discrimination among the cations in methanol–water solutions is poor [858]. Interestingly, monocarboxylic MCM mediate transport of M^{2+} as 1 : 2 complexes or as ternary complexes using readily extractable species as counter-anions [856]. The dicarboxylic carriers, however, transport them as 1 : 1 complexes [856]. The influence of stirring rate on transport of M^{z+} by such MCM has been examined [765]. A reaction system, which is rate limited by diffusion and contains a dicarboxylic carrier and Sr^{2+}, showed a continuous variation of the transport rate (of Sr^{2+}) over the range 100–600 rev min^{-1} in the stirring speed. However, the system containing a monocarboxylic carrier and K^+ showed a plateau above approximately 300 rev min^{-1}, consistent with a rate-limiting interfacial process [765]. A kinetic model has been developed to describe the transport selectivities exhibited by a liquid membrane system incorporating such an MCM [857].

As revealed by a thermometric titrimetric study [859], the macrocyclic poly(aminocarboxylic) acids exhibit selectivity among M^{2+}. The stability of the Mg^{2+} complex of 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate has been found to be higher than that for the Ca^{2+} complex [860].

The X-ray structural analysis of Li^+(*sym*-dibenzo-14-crown-4)oxyacetate $\cdot 7.5H_2O$ has revealed Li^+ to be 5-coordinate through four neutral ethereal oxygen atoms and a water molecule [861]; the cation-coordinated water molecule stabilizes the carboxylate group and prevents the latter from coordinating with the cation. Complexation of M^+ and Ba^{2+} by *sym*-dibenzo-16-crown-5-oxyacetic acid, **CIX**, in 80 wt.% methanol–20 wt.% water has been investigated by calorimetry [862]; the pH dependence of the complexation has been studied in detail. Further investigation of cation selectivity by **CIX** in 99 vol.% methanol–1 vol.% water through potentiometric titrations has demonstrated that the ligand selectivity towards cations can be turned by simply adjusting the pH of the medium; for **CIX** in the neutral form, the selectivity order is $K^+ \geqslant Na^+ > Ca^{2+}$, while it is reversed ($Ca^{2+} \geqslant Na^+ > K^+$) for the deprotonated form [863].

Lipophilic crown phosphonic acid monoalkyl esters are capable of effecting an anion-independent competitive extraction as well as transport from acidic and neutral aqueous solutions [866]. Participation of the side-arm in M^+–crown phosphonate monoethyl ester complexes in $CDCl_3$ has been investigated by NMR spectroscopy [867]; the spectra of the Na^+ salt differ from those of Li^+ and K^+ salts. A thermodynamic and kinetic evaluation of the side-arm interaction has been made during a study of Na^+ complexation in 80 vol.% methanol–20 vol.% water for four monoionizable MCM possessing carboxylic or phosphonic acid methyl ester groups [864]. A study of the

stability constants (log K_1 for the ionized ligand and log K_2 for the free acid) for Na^+ complexation has led to the conclusion that the highest stability is achieved when the charge density of the anionic side-arm is located near that cavity space which is to be occupied by Na^+ [864]. The critical micelle concentrations of MCM carrying the $CH_2SO_3^-$ group are almost unaffected by the addition of Li^+ but affected (enhanced) only by the addition of K^+ [868].

Lipophilic 14-crown-4 derivatives carrying a nitrophenol substituent display an excellent Li^+/Na^+ transport selectivity [869]. Such MCM are also excellent extraction–photometric reagents for Li^+ [870]. A new chromogenic macrocycle, 1(2-hydroxy-5-nitrobenzyl)-aza-12-crown-4, can be used for the determination of Li^+ in blood serum and urine [871]. The liquid–liquid extraction of M^+ from water into 1,2-dichloroethane has been investigated for several chromogenic macrocycles possessing pendant phenolic chromophores [872]. The nature of the crown ring, of the pendant phenolic group, and the geometry between the crown ether centre and pendant phenolic group have been discussed in detail [872].

A novel spherand azophenol dye, shows Li^+-specific colouration with "perfect" selectivity [873]. In fact, "acidic" chromoionophores have shown tremendous potential in this regard [778]. The MCM possessing an intra-annular phenolic group act as efficient carriers for M^+ from a basic aqueous phase to a receiving aqueous phase across the dichloromethane membrane [874]. Novel chromogenic lariat ethers possessing a monobasic amine function show improved extraction of M^+ compared with their benzo analogues [875].

Novel proton-ionizable MCM synthesized by Bradshaw and coworkers [876] and studied by the Izatt–Christensen group, distinguish themselves from the majority of the anionic MCM in that the site of proton ionization is at one of the ring donor atoms (as in **CXLIV B**, Fig. 51). It is thus possible to control whether H^+ or M^+ is bound by the macrocycle through adjustment of the pH of the source phase during a three-phase transport study. The selective transport of K^+ through coupled H^+–M^+ transport for individual M^+ and for binary M^+ mixtures has been accomplished [876].

Interest in the M^{z+} interaction with calixarenes (resembling **CXVII A**, Fig. 47) continues [760,877–883]. Calixarene-mediated transport studies from multiple equimolar M^+ mixtures have revealed a general Cs^+/M^+ selectivity irrespective of whether the mixture consists of two, three or four cations [877]. This feature is unique. However, for the systems with a high Rb^+/Cs^+ composition, *p-t*-butylcalix[6]arene displays favoured transport of Rb^+ obviously because the cation flux depends, in part, on the relative concentrations of the cations in the source phase [877]. Introduction of the acetic acid units on *p-t*-butylcalix[4]arene leads to a new series of lipophilic

as well as ionizable compounds, all of which display the highest Ca^{2+}/M^{2+} transport efficiency [879]. These MCM display, in particular, very poor Mg^{2+} transport possibly because of a strong solventphilic nature [9] of this cation. Conversion of calixarenes into electrically neutral calixaryl derivatives [880–883] helps to modify the interaction trends but even then transport selectivity towards M^+ is displayed. A new lipophilic ether ester ligand derived from *p-t*-butylcalix[4]arene reveals Na^+ selectivity in the extraction experiments [881]. The ion-binding ability of various calixarene derivatives (ethoxycarbonylmethyl, carboxymethyl and ethoxyethyl etc. of calix[4]arene, calix[6]arene and calix[8]arene) has been studied through solvent extraction and three-phase cation transport through a liquid membrane. Strikingly, ethoxycarbonylmethyl derivatives of calix[4]arene, calix[6]arene and calix[8]arene exhibit selectivities for Na^+, Cs^+ and K^+ respectively [882]. The X-ray structural analysis of $[Na^+$-*p-t*-butylmethoxycalix[4]arene-toluene$][C_6H_5COO(AlMe_2)OAlMe_3]^-$ has been carried out; the MCM exhibits inclusion of both the cation and the neutral toluene molecule [883].

Category 8 MCM. Interest in polymer macrocycles continues [884–907] and a chapter on such MCM appeared in 1984 [65]. In addition to the chromatographic applications, complexation in homogeneous media, extraction and transport have been studied [65].

Competitive binding of a soluble ligand and polystyrene- or polymethacrylate-bound B15C5 and B18C6 with Na^+ and K^+ (as pic^-) in toluene, dioxane and THF has been monitored spectrophotometrically [884]. Proton-driven active transport of cations has been investigated through polyamic acid membranes incorporating a crown ether moiety [886]; for the polyamic acid/18C6 membrane, transport decreased in the order $K^+ > Cs^+ > Na^+ > Li^+$. Quantitative evaluation of the ion-binding characteristics of poly(4′-vinylbenzo-18-crown-6) has been made [887]. The ion-binding abilities of polymeric chiral crown ethers have been studied following extraction of M(pic) from water into dichloromethane [888]. The complexation of K^+ and Cs^+ salts by polyamides containing DB18C6 moieties in the backbone has been investigated by ^{13}C and ^{133}Cs NMR (in DMSO-d_6) [889].

The ionic conductivity of polymer complexes has been investigated in detail [890–894]. The morphology and ionic conductivity of polymer complexes formed by segmented polyether poly(urethane urea) and $LiClO_4$ have been investigated [890]. The effects of polymer structure and incorporated salt species on ionic conductivity have also been studied for the complexes of aliphatic polyesters with LiNCS, NaNCS or KNCS [891]. A correlation between the ionic conductivity and dynamic mechanical properties of the complexes formed by a segmented polyether poly(urethane urea) with $LiClO_4$ has been suggested [892]. The conductivities of solid complexes of $LiClO_4$

with poly {[ω-methoxyhexa(oxyethylene)ethoxy]methylsiloxane} [893] and cross-linked polymers of α-methacryloyl-ω-methoxypoly(oxyethylene)s [894] have been examined.

Crown polymers are synthesized essentially by the traditional polymerization methods such as the vinyl polymerization, polycondensation, and the polymer reaction. A new method based on plasma polymerization has recently been reported [897], wherein DC18C6 has been "polymerized" on an acetylcellulose membrane by a glow discharge plasma; the membrane exhibits K^+ selectivity in ion transport.

The extraction of M^+ with polymer bearing pendant photoresponsive crown ethers has been investigated [898]. The complexation of poly(crowns) with photodimerizable groups has also been investigated [899,900] and an enhanced cation-binding ability via a photochemical template effect has been observed [900]. The cation binding of polymers carrying crown ether moieties as binding sites and cinnamoyl moieties as photodimerizable pendant groups has been studied and Rb^+ selectivity can be highlighted [901]. The photoinduced membrane potential changes for poly(vinyl chloride) membranes entrapping photoresponsive derivatives have been investigated in detail [902–904].

A poly(crown ether)-immobilized silica has been noted to behave as a stationary phase for reversed-phase liquid chromatography as well as ion chromatography [905]. The extraction of 1 : 1 electrolytes from aqueous solutions by resins containing DB18C6 as anchor groups has been investigated [906]. A detailed analysis of the pressure vs. area behaviour of Langmuir films of poly(4′-vinylbenzo-18-crown-6) spread on pure water and aqueous solutions of M^+ salts has been carried out [907]; the affinity of the polymer for M^+ at the air–solution interface resembles that of the monomeric analogue (B18C6) in solution whereas it is the reverse of that of the polymer in aqueous solution.

Category 9 MCM. Spherands and related molecules [908–914] continue to be investigated. The free energies of complexation of M^+ with five new spherands and three new hemispherands (resembling **CXXVI** and **CXXIX** respectively) have been determined [908]; the X-ray structural analysis of the hydrated NaBr and $CsClO_4$ complexes has also been carried out [908]. The thermodynamic and kinetic parameters for complexation of Li^+ and Na^+ (as pic^-) with some spherands in $CDCl_3$ have been determined [910]. The free energies of complexation of M^+ (as pic^-) with several bridged hemispherands have been determined [911]. This study also reveals interesting structural recognition factors for the congener pairs such as Na^+/Li^+, Na^+/K^+, K^+/Rb^+ and Rb^+/Cs^+. For anisole spherands, molecular mechanical calculations on the complexation of Li^+, Na^+ and K^+ have revealed [912] a high

selectivity for Li^+ and Na^+ compared with that for K^+, in agreement with experimental observations. The latest additions in this group are the cryptahemispherands, which are half spherand and half cryptand [913,914]. The X-ray crystal structures of several M^+–cryptahemispherand complexes have been determined and these MCM are shown to be highly selective as well as strongly binding hosts for M^+ [914].

The complexation of the veratrole analogue of phenoxyl-labelled B15C5 with M^{z+} in frozen solutions [915] and of the chiral spin-labelled crowns with K^+ [916] has been investigated by ESR. For MCM incorporating the oxathiane unit, the stability constants of complexes with Na^+ and K^+ have been determined potentiometrically in methanol [917]. For an anthraceno macrocycle, important alterations in conformation are shown to be induced by M^+ complexation which greatly affect fluorescent emission and photochemical regioselectivity; the X-ray structural analysis of its $NaClO_4$ complex has also been carried out [918].

The MCM 1,4,7,10,13-pentaoxa[13]ferrocenophane (an analogue of 15C5 incorporating a ferrocene moiety) has attracted considerable attention [919–921]. The X-ray structural analysis of its NaNCS complex reveals that the Na^+ stays paired with the counter-anion while the iron atom of the ferrocene moiety does not take part in coordination [919]. Upon electrochemical oxidation of this MCM, an abrupt decrease in the ion-binding ability takes place [920]. Electrochemically switched cation transport across a dichloromethane liquid membrane using this MCM has been investigated [921]. Such a method is apparently an efficient mode for the conversion of electrical energy into a chemical concentration gradient [921].

The complexing behaviour of new MCM, incorporating a ferrocene unit at 1,2- or 1,3-positions, towards M^{z+} has been evaluated through solvent extraction [922]. As indicated by fast atom bombardment mass spectrometry, two novel metallocene bis(crown ethers) derived from ruthenium and iron, are found to exhibit an exclusive K^+ selectivity over Na^+ or Cs^+ in intramolecular sandwich-type complexation [923]. The variety of ferroceno macrocycles has been extended through the synthesis of oxo-ferroceno-crowns and lariat-ferroceno-crowns; the complexation potential of the former towards Na^+, K^+ and Ba^{2+} has been evaluated through solvent extraction [924] and that of the latter through the synthesis of M^+ complexes [925].

A novel Schiff base bis(crown ether) has been designed to incorporate recognition sites for M^+ and transition metal guest cations [926]. The M^+ complexing ability and selectivity of a novel soluble copper phthalocyanine possessing four B15C5 moieties have been studied through extraction into dichloromethane; this MCM exhibits K^+/Na^+ selectivity [927]. Macrocycles incorporating B15C5 and B18C6 moieties coupled to a protein, bovine serum albumin, have been studied with a view to monitor changes in

conformation of the protein upon (i) conjugate formation and (ii) addition of Na^+, K^+ and Ca^{2+} to the crown ether moieties of the conjugate; K^+ and Ca^{2+} cause a decrease in the α-helical content of the cis conjugate while Na^+ exercises no perceptible effect [928].

The detailed structural results of the LiNCS–**CXXXVI** [929] and KNCS–**CXXXVI** [930] encapsulates (sandwiches) synthesized earlier [653] have become available. Lipophilic bicyclic multidentates, similar to **CXX-XVII**, behave as exceptionally strong binders for Na^+ [931]; the Na^+ complexes are stable even when refluxed for several hours in an acidic medium. These MCM indeed function as lipophilic cage ligands and form stable Na^+ complexes in non-polar media even for highly hydrophilic and poorly polarizable anions [932]. The ^{13}C and ^1H two-dimensional NMR characterization of the $NaClO_4$ complex of one such MCM has been made [933]; the ^{13}C NMR spectra and relaxation time measurements for different solvents revealed the absence of any specific solute–solvent interactions. More recently, the X-ray structural analysis of this complex has revealed Na^+ to be embedded in a non-symmetric cubic cage [934]. Cation transport studies across a liquid membrane incorporating a lipophilic bis(monoaza-12-crown-4) derivative exhibit extremely high Na^+ selectivity which can easily be controlled by the pH of the aqueous phase [935]. The complexation behaviour of novel bis(crown ethers) consisting of a benzo crown unit and a monoaza crown unit is analogous to that of the lariat monoaza crown ethers rather than that of bis(benzo crown ethers) [936]. The complexing ability of novel macrobicyclic compounds containing a nitrogen atom in the intramolecular bridge has been evaluated towards M^{z+} through stability constant determinations and extraction studies (dichloromethane–water) [937].

The X-ray structural analysis of the K(pic) complex of a tricyclic MCM **CXLV**, viz. $[K_2(\mathbf{CXLV})](pic)_2$, reveals [938] that each K^+ is 10-coordinate and is charge separated from pic^- (cf. structural analysis of [K(DB30C10)]I [147] and [K(DB30C10)]NCS [148]).

E. APPLICATIONS

The applications of macrocycles in chemical synthesis are mainly those involving the use in concealing the spherical cation from the reaction system and yielding, consequently, the activated counter-anions (naked anions). The latter act as powerful nucleophiles. The subject has been repeatedly reviewed [48,58,939]. Activated anions so generated have also been reported in the use of anionic conductors [940] that may lead to the industrial utility of the MCM. Separation of organic enantiomers with the help of chiral macrocycles is also a procedure more relevant to synthetic chemistry. This work involves chiral MCM synthesized and studied mostly by the Cram group [398,941]. These topics do not lie within the scope of the present article.

Analytical applications of the MCM are receiving increasing attention [77,942,943]. MCM, in general, render M^{z+} ions soluble in non-polar media. Thus the extraction and transport behaviour of M^{z+} has found applications in their analytical chemistry, even with low charge density cations such as Cs^+. The approach is to extract and concentrate the M^{z+} from an aqueous phase to an organic phase using an appropriate MCM and to determine M^{z+} by flame photometry or atomic absorption. Ba^{2+} has, for example, been separated from the rather closely related Ca^{2+} [310] and Sr^{2+} [311] using 18C6 and DB24C8 respectively. Separations using MCM have also involved chromatographic techniques with porous chromatographic columns [944–946] and miscellaneous devices [947].

The addition of M^{z+} to an MCM carrying a suitable chromophoric substituent (or an MCM in conjunction with a dye) may cause a change in colour leading to an appropriate analytical application [778]. Thus, bromocresol in conjunction with 18C6 has been used [948] for the determination of K^+. Nishida et al. [588] determined Li^+ and Ca^{2+} using fluorescent macrocycles while Sanz-Medel et al. [949] determined K^+ with 18C6 using a highly fluorescent counter-anion (eosin).

The phenomenon of transport has led to the fabrication and use of ion-selective electrodes. Initially, the electrodes were developed for Ca^{2+} and K^+ because the amide acyclics (for Ca^{2+}) [950] and naturally occurring antibiotics such as valinomycin (for K^+) [951–956] were appropriate as highly selective sensors. Soon crowns such as DB30C10 were also found [957–959] to be selective sensors for K^+. Subsequently, crowns [960,961] and especially the bis-crowns [439,444,445,962,963] were employed in K^+ electrodes. Now there exist electrodes for the not-so-strongly complexing Cs^+ [443,444] as well as for the rather anionphilic Na^+ [439]. The Li^+ selectivity of a liquid membrane electrode, based on DB14C4, is enhanced through the addition of triphenylphosphine oxide [964].

It is difficult to organize a set of conditions favourable to effective complexation of the divalent cations with MCM. For this reason, MCM-based M^{2+} electrodes have not proven useful as yet. Recently, the design of MCM suitable as ionophores for ion-selective electrodes (in terms of the carrier hypothesis, emphasizing the balance needed between maximum selectivity and a fast response time) has been discussed [965].

The use of MCM shows promise in the separation not only of the closely comparable cations such as Ca^{2+} and Sr^{2+} [966] but also in isotopic enrichment, with Na^+ [967] and K^+ [968]. The redox character of some anions has been made amenable to analytical work through complexation of the counter-cation; $Fe(CN)_6^{3-}$ through complexation of K^+ with, for example, 18C6 [969].

F. CONCLUDING REMARKS

In the late sixties crowns were the known popular macrocyclic multidentates which were capable of efficiently complexing M^{z+} ions. Soon it was realized that they are also capable of discriminating one M^{z+} ion from another in solution [142,392]; the crowns also discriminated between cations such as Na^+ and K^+ in the solid state although this was not realized during those early stages of the work [970]. The complexation data for the M^{z+}–crown systems, in both phases, was then understood in terms of the ion–cavity radius concept.

Since the early seventies, workers became increasingly conscious of improving the solution selectivity of these multidentates through structural changes. This led to the synthesis of MCM with numerous types of substituents on the crown ring and/or with fused aromatic moietie(s) and an ever-increasing class of crown-related macrocycles containing donor atoms other than oxygen. More information, unfortunately, was obtained concerning the variety of macrocycles than about the finer details of their discriminating power towards M^{z+}.

Until now, there has been a limit on the development of the subject because the ion-cavity concept prevails for solving all problems (even for modified macrocycles). We realized [9,11] quite early that though this concept does play a role, in particular towards M^{z+}–MCM stability in solution, the counteracting effect of the charge neutralizer is also important (which has recently been found [723] to be true even with complexation kinetics). In addition, the cation selectivity of a crown within and between M^+ and M^{2+} is dependent even more on the solvent medium. This determines the solvation of the ions and that of the macrocycle. It also depends on the structural features of the latter, such as donor number and ring substituents, so that the superimposed contributions of M^{z+}–crown, M^{z+}–anion, M^{z+}–solvent and crown–solvent interactions make the entire picture much more complicated than usually visualized. The solvation effects on M^{z+} and MCM become more important as the size of the cation decreases. Consequently, the interaction stoichiometry [236] and the selectivity sequence for a given series of cations (e.g. ref. 243) may even be totally different from what is expected. Although extraction and transport studies on crowns and crown-related macrocycles have usually been carried out (and had to be carried out) using organic salts as substrates, the equilibrium constant studies with the latter have largely been neglected. We expect the effects of these anionic species on M^{z+}–MCM complexation to be more pronounced and easier to rationalize.

Towards the late seventies, various "branded" MCM were introduced. These include bridged, polymer crowns, anionic, spin-labelled, lariats and

finally the spherands. An intermolecularly bridged crown yields practically the same 1 : 1 (anion paired) and 1 : 2 sandwich (charge separated) species with M^{z+} through its molecular component(s) as its components in the free state do. In view of their strongly complexing and hydrophobic features, these MCM appear to promise potential towards their use in ion-selective electrodes. The lariat ethers offer grafted flexible neutral arm(s) which cooperate towards M^{z+} complexation through a cavity. An adequately long flexible side-arm on the crown ring, which can be involved in cooperative complexation from the axial side, contributes significantly towards the stabilization of the M^{z+}–MCM complex by enhancing the total number of binding sites of the molecule and also by preventing the anionic species from destabilizing the complex from the axial side(s). The molecules with nitrogen-based arms, in particular, and which can protonate and deprotonate at the tertiary nitrogen(s) appear to show promise for active transport through proton exchange.

Chemically anionic MCM differ from the lariats in the sense that while binding the cation in the cavity of the macrocyclic part, they function as charge neutralizers and the molecule as a whole behaves as a cation exchanger. The pH dependence of their cation exchange makes them even more useful (cf. ref. 578). The anionic MCM possessing more than one carboxylate function are, in general, M^{2+}/M^{+} selective (while those containing more than one amide in the ring appear, in particular, selective for Ca^{2+}). Among anionic MCM, the calixarenes are unique in that (i) they display transport selectivity for the lowest charge density Cs^{+} and (ii) transport of a medium-preference cation can be so dependent on its own concentration that it may ultimately overtake the most highly selected cation. Spherands are improved cryptands (which are mainly bicyclic species) in which the cavity is rigid as well as enforced making them unusually efficient for binding small cations. Spin-labelled MCM and those carrying NMR-active nuclei as donor sites are in particular the newer exemplary MCM which offer the applicability of additional techniques for the study of M^{z+}–MCM complexation. The polymer MCM, wherein the MCM function is cooperative, are also powerful complexing species of possible potential for phase-transfer studies.

Since the early eighties in particular, research has focused on the extraction and transport ability of the MCM towards M^{z+}. However, the results are still inadequate to rationalize the solution chemistry of M^{z+} under phase-transfer conditions. The broader relationship of the M^{z+}–MCM log K values with log K_{ext} as well as their transport features is nevertheless being understood; the major effects of the minor log K differences towards transport behaviour are, for example, being noticed. Interest is increasingly growing towards the study of synergistic effects. Competitive transfer studies

involving binary cation mixtures in the source phase are attracting attention wherein transport of a cation is dependent on the nature of the co-cation and is different from the one when it is present alone. The anions influence M^{z+} transfer across the boundary of two immiscible phases.

One is intrigued that there is no direct study of MCM vs. anion preference of M^{z+} through monophasic lipophilization (solubilization) studies of M^{z+} salts in non-polar media under "solventless" conditions. This work could offer information on direct MCM vs. anion competition, in the interests of understanding the Lewis acid status of the individual M^{z+}. We are currently undertaking this type of work using MCM as well as conventional bidentate and multidentate acyclics.

The broader conclusions to be drawn from the solid state results are that the interaction and interaction stoichiometry of the M^{z+} and MCM are essentially a function of the charge density (charge/radius ratio) of the M^{z+}, the state of charge localization of the counter-anion (which determines its pairing with the M^{z+}) and the flexibility as well as basicity of the MCM cavity. In support of these principles, the ion–cavity concept is almost insignificant. This is most conspicuously illustrated by the formation of, for example, the anion-paired 1 : 1 or 2 : 2 complexes of B15C5 with Cs(pic) or Rb(pic) [1 : 1], $Ba(pic)_2$ [1 : 1] and $Ba(dnb)_2$ [2 : 2] instead of the expected 1 : 2 complex for each.

Until now, structural aspects of the Li^+–crown complexes were less well known. Recently, information on diverse Li^+–crown systems has appeared. There are apparently widely differing interactivity patterns for this cation. A number of systems represent partial dehydration of Li^+ by the crown, which is also bonded to the water protons. The overall MCM/anion preference of a cation for a given MCM and anion can vary understandably, reflecting the Lewis acid status of the cation as seen, for example, through X-ray structural analysis of $M(pic)(B15C5)_x \cdot yH_2O$ ($M^+ = Li^+$ to Cs^+) systems. The screening of the solid state structural aspects of related compounds with several M^{z+} and a given crown-related MCM with a common anion has been initiated [472,473,498,503–505,817–819]. The work is worthwhile in the interests of understanding the interactive characteristics of M^{z+}.

The charge density of the cation can manifest itself in more than one way. The highest charge density Li^+ (or Mg^{2+}) may display self-complexation with a neutral ligand including water (solventphilicity or ligandphilicity [9]), a medium charge density cation such as Na^+ may display anion pairing in the complexed state (anionphilicity) while the lower charge density K^+ can exhibit strong ligandphilicity over anion pairing (ligand complexation [9,11]). Results for the lowest charge density Cs^+ may, however, be unexpectedly comparable to those of a cation such as Na^+ in that anion-paired complexes may be formed while Rb^+ may mimic Na^+ (Cs^+) or K^+ depending upon the effect of the counter-anion.

Interestingly, anions affect the conformation of the MCM ring even with the charge-separated sandwiches. For a given cationic moiety, it varies with different anions, but it has been less examined with the crown-related MCM.

Anion pairing of the complexed low charge density M^{z+} and consequent dimerization of the complexes was noted earlier [9] especially for NCS^- but later results revealed that "dianionic" substituents such as the carboxylate functions or even the neutral carbonyl functions of the MCM may make the 1 : 1 complexes behave as 2 : 2 in the crystal lattice. A new structural feature in the crystal lattice is dimerization which can arise through a molecule of water involving higher as well as lower charge density M^{z+}.

Of all the M^{z+}, the solvation features of Mg^{2+} are unique in that it undergoes enhanced solvation when it is covalently bound. Thus, Grignard's reagents freely solvate with feebly polar solvents (such as Et_2O and THF) [9]. Also, Mg^{2+} is more strongly solvated (with DMF) in a complexed state with a powerful MCM (15C5) [731].

Since K^+, Rb^+, Cs^+ and Ca^{2+}, Sr^{2+}, Ba^{2+} constitute those trios of cations for which the within-the-group difference in ionic properties is rather narrow, the job of chemical discrimination is really difficult. For the conventional ligands, the M^+ trio is only weakly interacting and the within-the-group discrimination is rather difficult; that of the M^{2+} group is, however, marginally possible [971]. The macrocycles have displayed a distinct superiority to reveal the discrimination for both trios. The role of O-donor crowns such as **B15C5** for the M^+ trio and MCM containing N-donors such as **LVII** and **LXXXVI** for the M^{2+} trio, is worth a special mention.

As noted for various conventional bidentate and polydentate ligands (work is in progress in our laboratories), Sr^{2+} mimics Ba^{2+} when the anion is weak and the ligand is strong but mimics Ca^{2+} as the anion is strong and the ligand is weak. When, however, the anion is highly charge localized and the ligand is also relatively powerful, the within-the-group discrimination for the trio Ca^{2+}, Sr^{2+}, Ba^{2+} is not possible as noted through a recent X-ray analysis of the systems $M(NO_3)_2$(DM18C6) ($M^{2+} = Ca^{2+}$, Sr^{2+} or Ba^{2+}) [685].

Cation selectivity through complexation in a homogeneous medium, extraction, or through transport using cyclic ionophores can have high analytical utility. Thus, using N-donors one can achieve selectivity towards the small cation of M^+ as well as of the M^{2+} series. Using O-donors use can be made of an enhanced selectivity towards the large cation of each series (but only up to K^+ (Rb^+?) for the M^+ series, as the Lewis acidity of Cs^+ is so diminished by the charge neutralizer that Cs^+–ligand interaction is weak even for oxygen). The cyclic ligands such as 18C6 or DC18C6 (the donor

ring basicity of which is not diminished by the acidic substituent and whose ring size is also suitable), however, provide a unique opportunity for selectively transporting the Cs^+ ion [364]. See also the selectivity patterns of calixarenes (vide supra and Section C (vii)).

The MCM carrying a dominant number of N-donors ensure M^{2+}/M^+ as well as small/large M^+ selectivity. Thus, while 18C6 is K^+/Ca^{2+} selective, **LXII** is Ca^{2+}/K^+ selective. Various special MCM yield special results. Thus, the multiloop **XLVIII** can ensure, for example, Na^+/Ca^{2+} selectivity in the solid state. For the pH-dependent MCM carrying ionizable substituents, M^{2+}/M^+ selectivity is (and has to be) fairly general; for such MCM, uniquely, the extraction sequences for M^+ can be modified even by a change of the non-polar solvent.

The initial screening studies with diverse new MCM are now becoming more intensive chemical investigations. Also, there is a greater emphasis on extraction and transport studies—work which can become more useful if, instead of focusing just on the most highly selected cation, the results are analysed for all cations under study. Extensive crystallographic investigations on related compounds are being undertaken for crown-related MCM, as for the crowns [970]. Even theoretical studies are being extended [770,912] to these systems.

ACKNOWLEDGEMENTS

We thank DST and UGC, New Delhi, for research grants to N.S.P. and A.V.B. respectively, and Dr. Pushpa Bagdi and Mr K.S. Sidhu for their help in drawing the figures.

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