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Consequences of the 'Pedersen Papers' on Crown Type Chemistry at Würzburg and Bonn Universities: From Heteroaromatic Crowns and Podands to Large Molecular and Crystalline Cavities Including Multisite Receptors, Cascade Molecules, Chromoionophores, Siderophores, Surfactant-Type, and Extreme Ligands

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Abstract. We thank the editors of this issue for the opportunity to present the historic development of crown chemistry at the Universities of Würzburg and Bonn in memory of C. J. Pedersen, the originator of the crown ethers. His legacy of science has tremendously stimulated research at both universities.

Key words. Crown-type compounds, podands, multisite receptors, chromoionophores, siderophores, surfactant-type crowns, large molecular cavities, crystalline hosts, complexation chemistry, crystal structures.

1. Introduction

1.1. GENERAL REMARKS

Evolution in chemistry is difficult to predict. The moment you finish a chemical experiment you hardly know whether you have only produced a boring compound or opened a door to a fruitful scientific future. Sometimes a primer from outside is required to bring your chosen course of science to detonation and ring in a new chemical era. We had this experience thanks to the discovery of the crown ethers by Charles J. Pedersen [1]. The memory of this lucky break in our research work unleashed by the revolutionary Pedersen papers on crown ethers in 1967 [2, 3] is still alive.

1.2. PREVIOUS HISTORY

In the period before Pedersen, one of the main interests of the Vögtle group was in cyclophanes [4], a general type of macrocycle incorporating aliphatic and aromatic ring segments (Figure 1). In particular, the efforts were directed to the study of highly strained [5] and multiply bridged [6] cyclophanes and heterophanes (cf. **1**–**5**)

This paper is dedicated to the memory of the late Dr C. J. Pedersen.

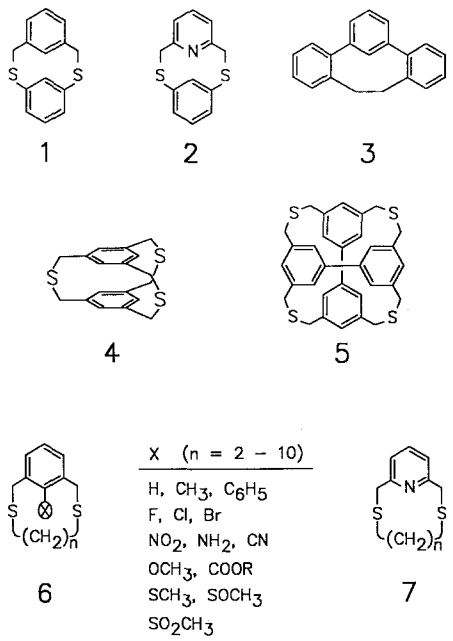


Fig. 1. Typical cyclophane-type macrorings of our pre-Pedersen era [4–8].

or similar macrocycles which were fitted with intraannular substituents with the aim of measuring their steric demands [7] (cf. **6**). In the case where these compounds contained heteroatoms, such as nitrogen, oxygen, or sulphur, the heteroatoms were only in the minority. On the other hand, some of the typical macrorings studied at that time embody a long (CH_2)-segment bridged in the 2,6-position via sulphur atoms across a pyridine nucleus (**7**) [8].

However, in the late sixties, the first signs of a macrocyclic complexation chemistry emerged from the research work of the Vögtle group. They relate to the compounds specified in Figure 2, i.e. macrocycles **8** [9], **9** [10] and **10** [11], and a macrobicycle **11** [12] with appropriately located sulphur, nitrogen and oxygen (donor) atoms, and a cavity. Correspondingly, **11** yielded a stable complex with Cu^{2+} and Hg^{2+} ions [12]. Thus these macrocycles may be considered a preliminary operation in preparing the ground for the development of crown chemistry to come.

2. Crown Research at Würzbury University (Vögtle, Weber) Stimulated by C. J. Pedersen

2.1. WHAT GAVE US THE IDEA?

In the strict sense, the prime Pedersen crown, dibenzo-18-crown-6 (**12**) [1–3] may be understood as a heteracyclophane [13] (Figure 3), but substitution of individual CH_2-groups in **7** at proper positions leads to a novel type of crown compound with heteroaromatic units incorporated in the macroring to meet a crown

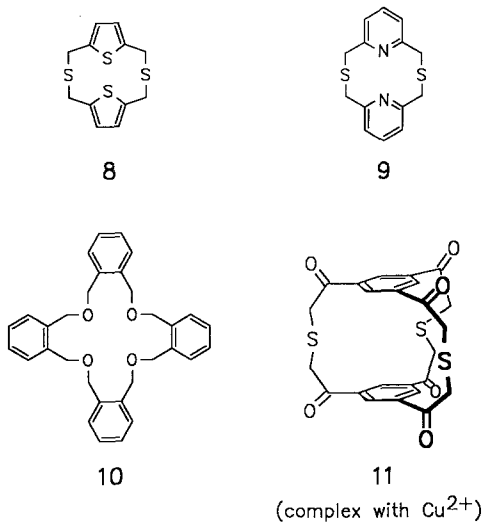


Fig. 2. The first signs of a macrocylic and three-dimensional complexation chemistry [9–12].

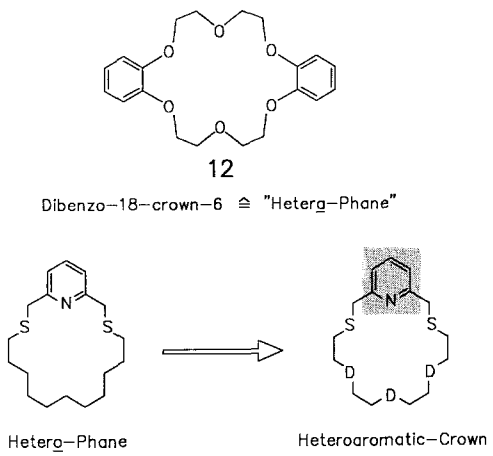
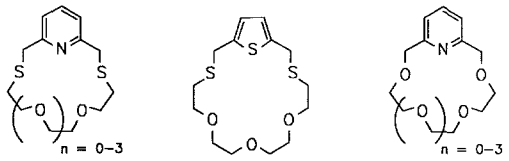


Fig. 3. The prime idea: from heterophane to heteroaromatic crown (D = donor hetero atom).

analogous arrangement of donor atoms such as that exemplified in Figure 3. By doing that, the cyclophane and the crowns get married, and the union promises much for the future. This is the initial break in our research that owed thanks to Pedersen's ingenious first papers [2, 3]. It was during the time at Würzburg University.

2.2 REALIZATION OF A NEW CROWN TYPE – THE HETEROAROMATIC CROWNS

Edwin Weber (now Professor at Bonn University) had the privilege of performing the marriage rites between cyclophanes and crowns. During the time under consideration (1973) he began his doctoral work [14] with Prof. Vögtle on exactly this



13 14 15

Fig. 4. First generation heteroaromatic crown compounds [15, 16].

heteroaromatic crown type compound (Figure 3). Since we had mastered cyclophane synthesis, the success came quickly. Within some few weeks the first compounds of the heteroaromatic crown class (**13**, **14**; Figure 4) had been prepared in the Würzburg laboratory. We realized that the compounds had quite unexpected complexation behaviour with respect to Na^+ ions, i.e. they easily solubilized $NaMnO_4$ into organic solvents, as contrasted with $KMnO_4$. Thus we had discovered a new efficient crown family (actually the first – and foremost – crown compounds synthesized in Germany). A paper for *Angewandte Chemie* was prepared, smoothly accepted, and we looked forward to its appearance [15].

Although we knew about the importance of our discovery, it hardly entered into our heads that at the same time somebody else could have had a similar idea that would lead him to the same matter. But the unbelievable became true. Just a few days before our paper on the pyridinodithia-crowns appeared [15], we became aware of a short note in the 'blue pages' (*Nachr. Chem. Techn. Lab.*) [16] referring to a talk by D. J. Cram indicating that he had worked on similar pyridino (all-oxygen) crowns **15** (Figure 4). Obviously the new heteroaromatic crown type has been developed independently in the two different laboratories. We were overcome by a fateful event of overlap in chemistry relating to the origin of research work.

Nevertheless we took advantage of the fact, having published the first real scientific paper in German and English editions [15] on the new heteroaromatic crown type having versatile complexation properties as illustrated in Figure 5 [17]. Due to the coexistence of hard (oxygen, nitrogen) and soft (sulphur) donor atoms, coordination to alkali/alkaline earth and transition metal ions is possible (cf. Ba^{2+} and Cu^{2+} complexes of Figure 5) giving rise to extended conformational re-arrangements.

2.3. FIRST USE OF INTRAANNULAR SUBSTITUENTS

Fortunately we did not suffer the same fate with the intraannularily substituted or modified crown compounds **16** and **17** (Figure 6) [18, 19], some of which were also described in our first paper [15]. Compounds **16** arise from **6** when the alkyl chain is replaced by a crown analogous oligo-ethyleneoxy segment. This crown type, or more generally speaking, the idea of intraannular substitution of crowns, became very important in chromoionophore design [20] and still lives on in the recent spherands of Cram [21] (another overlapping of interests between both research groups). Other crown constitutions developed at that early time are represented by formulae **18**–**20** (Figure 6) [19].

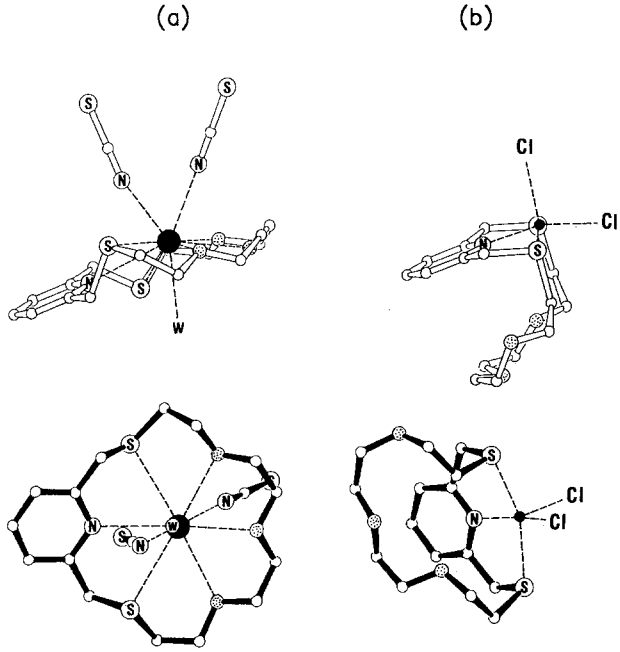


Fig. 5. Perspective views of the hydrated $Ba(SCN)_2$ (a) and the $CuCl_2$ complex (b) of dithiapyridino-18-crown-6 (**13**, $n = 2$; Fig. 3) from crystal structures (H atoms omitted) [17].

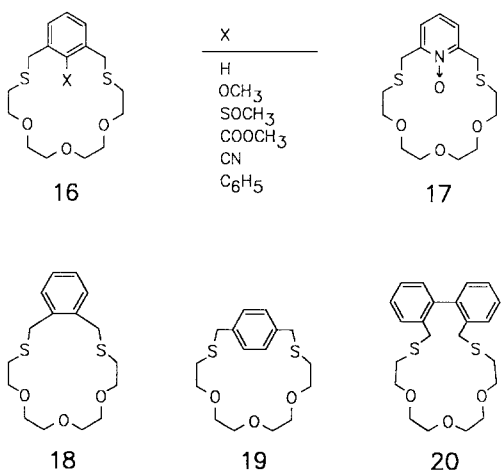
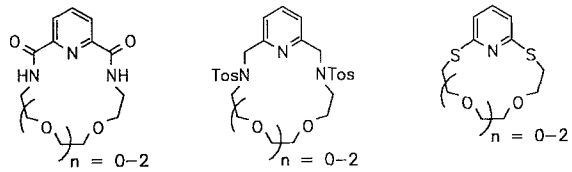


Fig. 6. Intraannularily substituted crown compounds and other early developed crown constitutions [18, 19].

2.4 HANDLING OF DONOR ATOMS AND LINKAGE POSITIONS

It is typical of the early period of our crown research that we used sulphur as a linking atom in a benzylic position (cf. Figures 4 and 6). This changed in subsequent work since nitrogen (donor) atoms such as those in **21** and **22** (Figure 7) were increasingly used to close the ring [19, 22]. On the other hand, sulphur



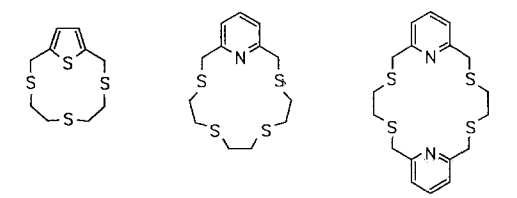
21 22 23

Fig. 7. Heteroaromatic crowns with modified linkage atoms and linkage positions [19, 22].

(donor) atoms were still used for ring closure, but rather in a non-benzylic position to yield heteroaromatic crowns **23** (Figure 7) of quite uncommon ring sizes [19, 22].

It was also Edwin Weber's work at the laboratory bench which replaced the oxygens in the oligoether segment (cf. **13**, **14**, etc.; Figure 4) by sulphur atoms, i.e. he synthesized all-thia and mixed thia-aza aromatic crowns, exemplified by formulae **24**–**26** (Figure 8) [23]. Replacement of the oxygens in the oligoether segment by nitrogen, such as in **27**–**29** (Figure 8), was undertaken by other members of the Vögtle group [22]. These heteroaromatic crowns with only thia and aza donors showed particular complexation properties in respect of transition metal ions [22, 23].

In addition to the mixed thiaoxa, thiaaza, and all-thia or all-aza crowns, we wanted to have crowns with oxygen and nitrogen (cf. **15**; Figure 4) or only oxygen donors. It was expected that they would behave as more efficient complexants for alkali and alkaline earth metal ions [24]. The first step into this direction was again undertaken by Edwin Weber. The key diphenol compound **30** of his synthetic approach (Figure 9), however, came from Pedersen's early work [3]. Thanks to that he succeeded in the synthesis of a large number of oxaaza and all-oxa crowns



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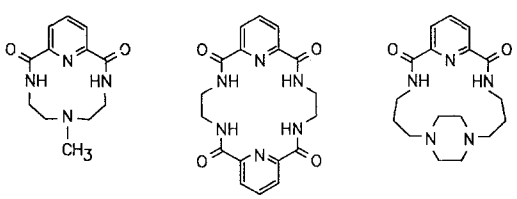


27 28 29

Fig. 8. All-thia, mixed thiaaza, and all-aza heteroaromatic crown modifications [22, 23].

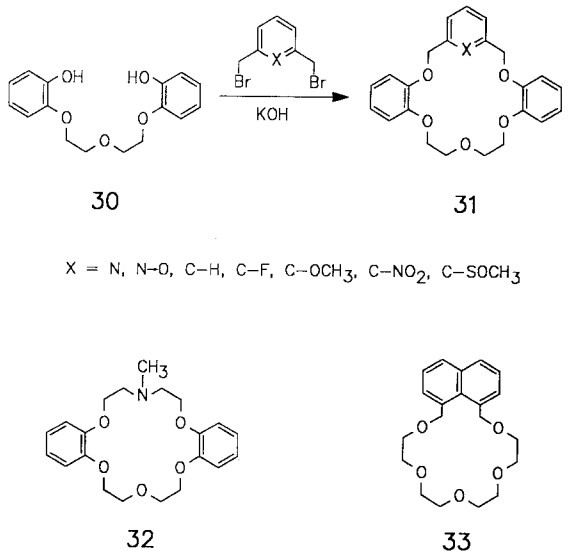


Fig. 9. Just as we thought! Synthesis of oxaaza and all-oxa (intraannularily-substituted) crowns [19] based on the 'Pedersen diphenol'.

exemplified in Figure 9 (**31**–**33**) [19]. For the most part, they showed strong binding of alkali and alkaline earth metal ions and useful solubility properties of their salts [19, 25].

2.5 THE NONCYCLIC VARIETY OF CROWN COMPOUNDS: PODANDS

The next innovative step of the crown research at Würzburg University stems again from a joint Vögtle/Weber idea. For application of crown compounds, e.g. as phase transfer catalysts, it would be an advantage to make cheap crown analogs available [26–28]. What about using noncyclic analogs of crowns (later called 'podands')? They allow the saving of a ring formation stage and reduce the preparation to a conventional synthetic problem. However, we knew from Pedersen's work [29] that simple glymes were not capable of efficient complexation. If we refined the glyme terminals by so-called strong and rigid donor end-groups, such as quinoline residues, would it give the desired effect? We did the experiment and, in fact, it worked out fine.

The first compounds of this new ligand class were the bis-(quinolino)oligoether **34** and its pyridine analog **35** (Figure 10) [30]. They yielded a great many stoichiometric crystalline complexes with different alkali, alkaline earth, and transition metal salts. Thus the door to the promising field of non-cyclic crown analogs – termed podands [31] – was opened.

It took us only a short time to synthesize a large number of podands with different end groups and chain lengths (cf. **36** in Figure 10) [32], and to study their complex formation properties [33, 34]. The complexes gave very interesting crystal structures [32, 35] ranging from butterfly conformations to helices and spheres (Figure 11a–c) [36–38]. Consequently, a so-called 'end group concept' [32, 39] was

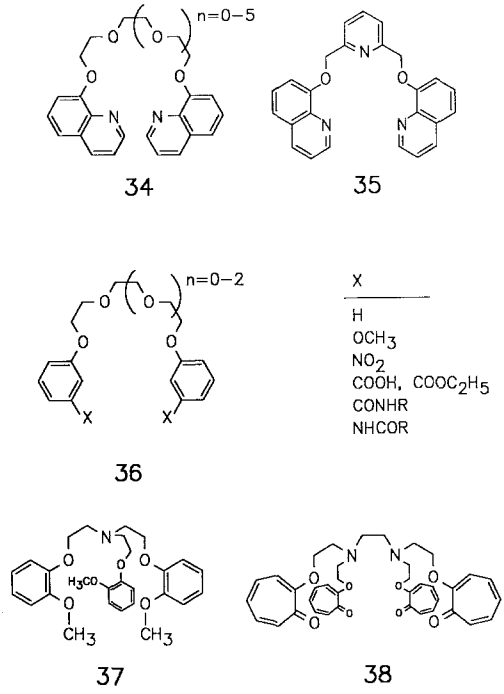


Fig. 10. The noncyclic crown/cryptand version (podand and open-chain cryptands) [30, 39, 46, 47].

developed, which made an efficient podand design possible [40–44]. It is still being used on other places to discover new ion carriers [45].

The same principle was applied a little later to tripod and tetrapod constitutions such as are exemplified by formulae **37** and **38** (Figure 10) [46, 47]. Due to their strong complexation with alkali and alkaline earth metal ions, and for reasons of topology, they were termed 'open-chain cryptands' [32]. Indeed, crystal structures of the complexes show efficient wrapping of the cation (Figure 11d) [35].

2.6. THE TENTACLE APPROACH: OCTOPUS MOLECULES

Possibly the most popular compounds developed during the joint Vögtle/Weber era were the 'octopus molecules' (Figure 12) [48]. To some extent they relate to the noncyclic cryptands mentioned above but they were synthesized earlier. A characteristic of this compound type is the high number of coordination 'tentacles' (e.g. six in **39**) which make them efficient complexants and carriers for alkali and alkaline earth cations. The phenomenal structure, resembling that of an octopus (though not in the number of tentacles), has imparted the nick-name 'octopus molecule'. The term is apt because the donor atoms act like the suction cups with which a real octopus grasps food (Figure 12). For compound **39**, the meal consists of metallic ions and, as mentioned, its appetite for particular main Group I and II cations is voracious. Later, it was found that 'octopus'-type molecules are also hosts for uncharged organic molecules [49].

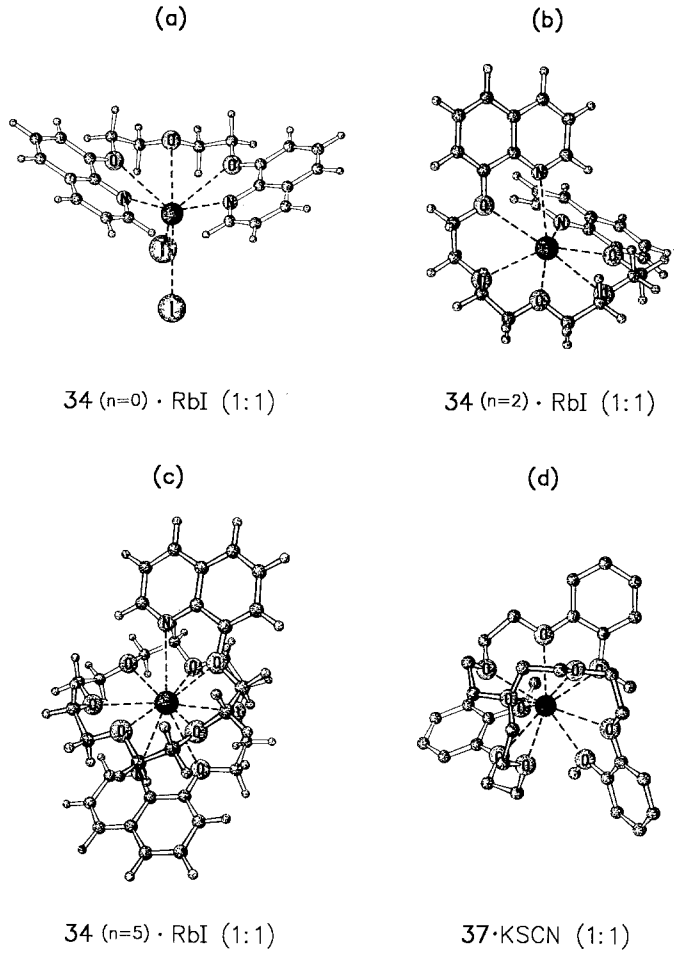


Fig. 11. (a) Butterfly, (b) helical, (c) spherical, and (d) wrapping complexation of metal ions by non-cyclic crown compounds (podands; crystal structures) [35–38].

At the end of 1975, the Vögtle group moved from Würzburg to Bonn University. In 1976, Edwin Weber finished his doctoral thesis [14] on the various topics mentioned above and began his own work. From now, we have two independent research groups working at Bonn. In the following, we will look separately into the highlights these two groups have achieved from about 1976 (Weber 1978) up to the present time, stimulated by C. J. Pedersen's work.

3. Vögtle Group Research at Bonn University

3.1. NEW PLACE, NEW TOPOLOGY, NEW BUILDING BLOCKS

On the one hand, the removal of the Vögtle group from Würzburg to Bonn University became manifest in a topical extension oriented along the three-dimensional cryptands [50–53]. On the other hand, a logical continuation of the previ-

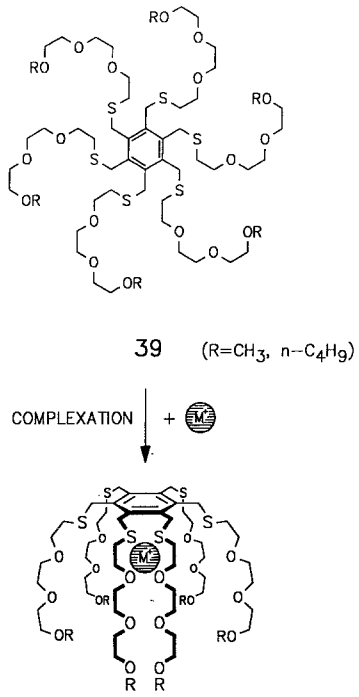


Fig. 12. Imitating the animal: 'octopus molecules' grasp cations [48].

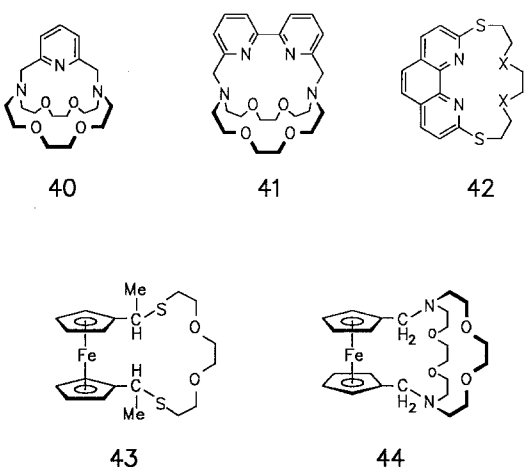


Fig. 13. Crowns (coronands) and cryptands incorporating pyridino, bipyridino, phenanthrolino, and ferroceno subunits [50, 51, 55, 58].

ously pursued course of applying new building blocks and donors is also evident [5, 52, 54–58]. This is expressed in Figure 13 showing examples of the first pyridino and bipyridino cryptands (**40** or **41**) to be synthesized [50, 51, 53] as well as of phenanthrolino crowns (**42**) [55] and of crowns/cryptands (**43**, **44**) for the first time

incorporating a ferroceno unit [58]. These particular building blocks are still important structural parameters in recent host design [59, 60].

Another new building block development refers to the use of structural constituents, as in natural bioactive compounds or synthetic drugs. The underlying idea was to use crown modification to equip ordinary pharmacophoric substances with cation selectivity in order to make them affine to particular cation-containing tissues, such as those in bones, or to effect local ion concentrations. Thus, a series of crowns and podands bearing haptophoric and pharmacophoric groups (papaverin, adrenalin, apomorphin, cinnarizin, procain, etc.) have been synthesized and studied [61–65]. Examples are given in Figure 14 (**45–49**).

Moreover, the typically amphiphilic lipids, as another class of natural compounds, were also modified in a crown or podand analogous manner to give 'hydrophilic lipids' (**50**, **51**; Figure 14). These podands, based on the glyceryl backbone, show interesting cation carrier properties [66].

3.2. COLOR RESPONSIVE CROWNS: CHROMOIONOPHORES

Pedersen had shown in his initial papers [2, 3] that the UV spectrum of dibenzo-18-crown-6 (**12**, Figure 3) is slightly effected by complexation, depending on the cation

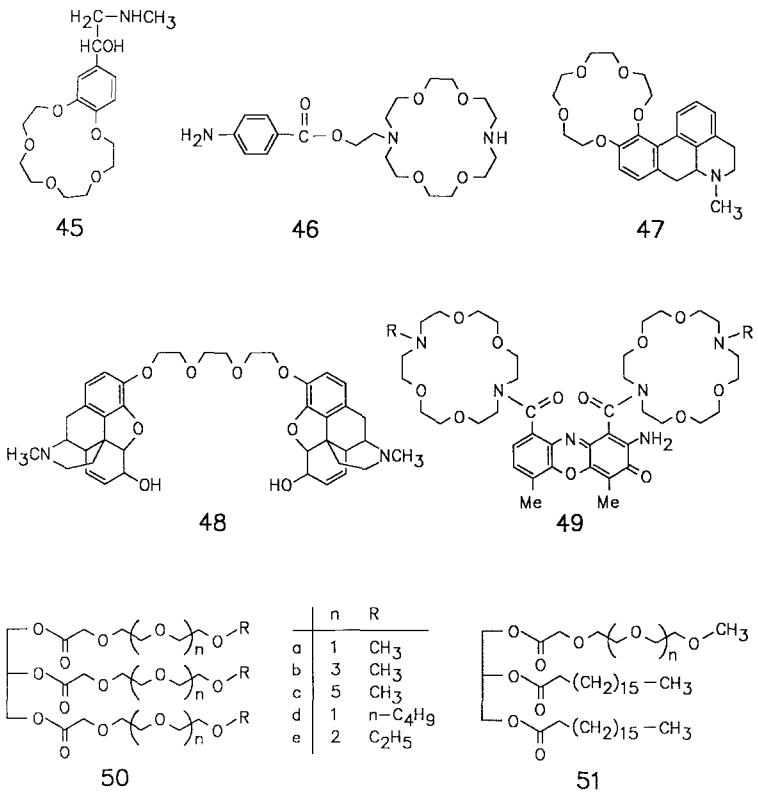


Fig. 14. Natural compound and drug related crowns/podands [61–66].

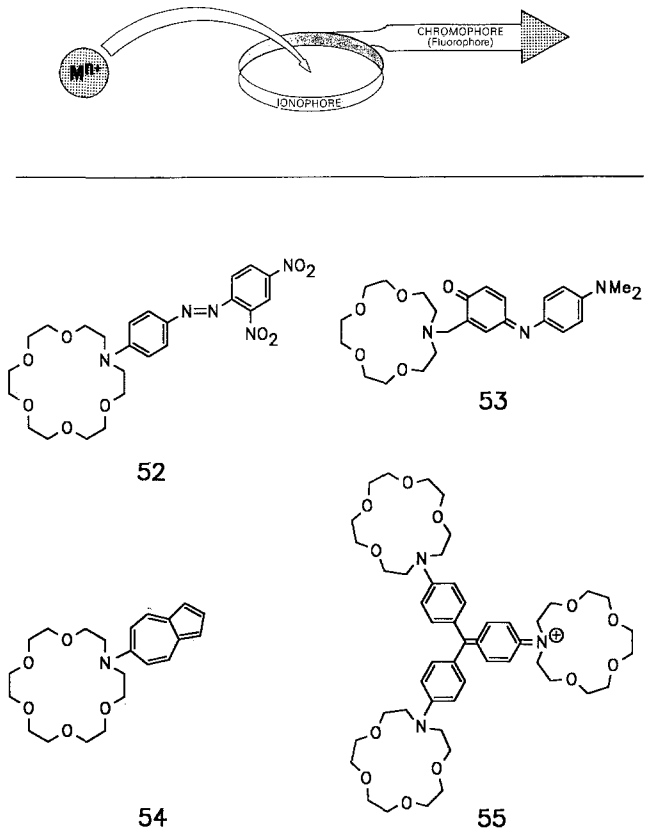


Fig. 15. Chromoionophores: molecular construction and examples of compound [20a, 67–71].

type. He used the property as a method for establishing complex formation [3]. Stimulated by this early work of Pedersen, the chromoionophores were developed [20a]. This particular class of dyestuff-analogous crown compound is based on the general idea of making selective cation complexation of crown compounds visible through a color effect in the same molecule [67]. It requires, besides the ligand-typical (coordination active) part, a chromophore in the molecule, and an electronical coupling between both, as illustrated in Figure 15.

A number of chromoionophores were designed on the basis of this principle. They include chromophore elements such as azo, quinone, quinone imine, azulene or cyanine groups [68–71]. Typical examples of compounds are depicted in Figure 15 (**52–55**). Examples of the chromophore effect that such compounds provide on the addition of different cations are shown in Figure 16. The quinone imine type chromoionophore **53** gives significant bathochromic shifts with enhanced extinction [69]. After this we proceeded to chiral dyestuff crowns [72] which were expected to give different color effects with guest enantiomers.

Independently, Japanese scientists developed similar types of chromoionophores [73], but with proton ionizable (acidic) groups [20].

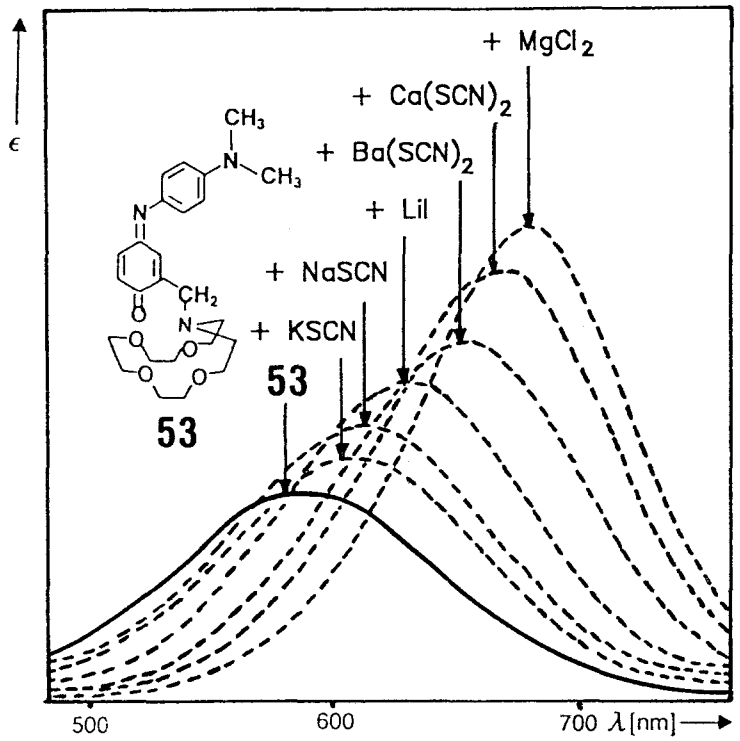


Fig. 16. Selective ion determination via cation selective light absorption: bathocromic shifts upon addition of salts to a solution of the chromoionophore **53** in acetonitrile [69].

3.3. BEGINNING OF THE SUPRAMOLECULAR ERA: COMPLEXATION OF UNCHARGED GUEST MOLECULES BY CROWNS AND PODANDS

It was also Pedersen who stimulated our initial work on crown and podand chemistry with uncharged guests. In one of his early papers [74], he mentioned the isolation of crystalline complexes between dibenzo-18-crown-6 and thiourea or related compounds but their structures remained unclear. More remarkable is that a crystalline urea complex was not included, although Pedersen stated that he had found enhanced solubility of dibenzo-18-crown-6 (**12**, Figure 3) on addition of urea [74].

To succeed with crystalline urea and thiourea complexes became a spur to us because of the importance of these molecules. Fortunately, we were successful in isolating the first crystalline urea complexes of oligoethers which were simple podands [75, 76]. We were even able to solve the crystal structures of the corresponding thiourea complexes (Figure 17a, b) [77, 78]. This was the beginning of our complexation chemistry with uncharged molecules as guests [79].

Following on from this we prepared and studied a series of further complexes of crowns, heterocrowns, and podands with uncharged OH- NH-, CH- and SH-containing guests such as dimethyl sulfate, anilines, hydrazines, phenols, water, and others [80, 81, 82]. Typical examples of complex structures involving 18-crown-6 [83, 84] are illustrated in Figure 17c and d. Some of these complexes were used as

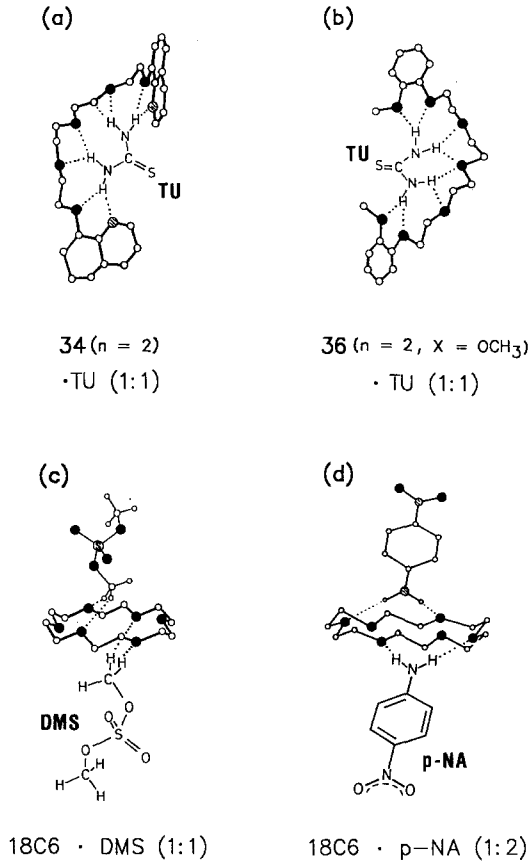


Fig. 17. Crystal structures of typical uncharged molecule complexes of podands (a, b) and 18-crown-6 (c, d) of the early supramolecular period (H-bonded complexes, H-bonds dotted) [74, 78, 82, 83].

reagents with the complexed species exhibiting modified solubility and reactivity properties [85–87].

3.4. DESIGNED HOST TOPOLOGIES FOR UNCHARGED MOLECULE COMPLEXATION

Believe it or not, even the three-dimensional host structures shown here owe their origin to some degree to Pedersen if one considers his 'lanterns' [32] and other compounds mentioned in one of his many patents (see Ref. [1]). It is also foreshadowed in his work [32] that trigonal host symmetry is something fundamental. Despite this support from basic principles, the development of hosts which will specifically complex organic uncharged molecules is difficult to manage [79, 88].

In this respect, one of the successes of the Vögtle group refers to the synthesis of host molecule **56** [89] – a macro-cyclic hexa-amide with inherent three-fold symmetry (Figure 18). Previous host molecules of this type had two-fold symmetry, which makes it possible to achieve a relatively simple synthesis from two molecular halves [88]. Hosts such as the ones we consider here, having a three-fold molecular axis,

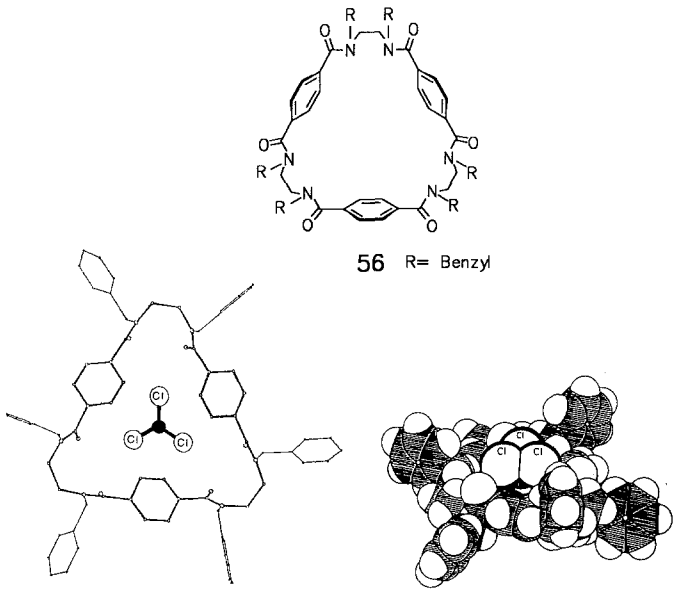


Fig. 18. A host with threefold symmetry (**56**) recognizes chloroform to give a crystalline inclusion compound selectively [89, 91].

are much more difficult to synthesize. In recompense, the 'endoreceptor' **56** yielded highly selective inclusion complexes with haloform-type guest molecules (CHX_3) [89]; to our knowledge this is one of the first uncharged host–uncharged guest complexes to have been discovered. The complexes are even stable in solution, as measurements using ion selective electrodes demonstrated [90]. The crystal structure of the $CHCl_3$ complex shows a well-fitting supramolecular host–guest aggregate (Figure 18) [91]. Clearly, the correspondence of trigonal symmetry between host and guest is operating here.

Another interesting host topology was materialized in the form of molecules shaped like a basket or a cup [92]. Examples are given in Figure 19 (**57**, **58**). Basket compound **57a** forms a stable inclusion complex with dioxane [92].

In subsequent work it was a challenge to proceed from a molecular basket to a closed cavity [93, 94]. This requries the use of two trivalent building blocks (**B**) that

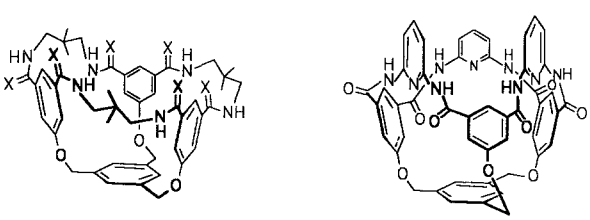


Fig. 19. Basket-type hosts [92].

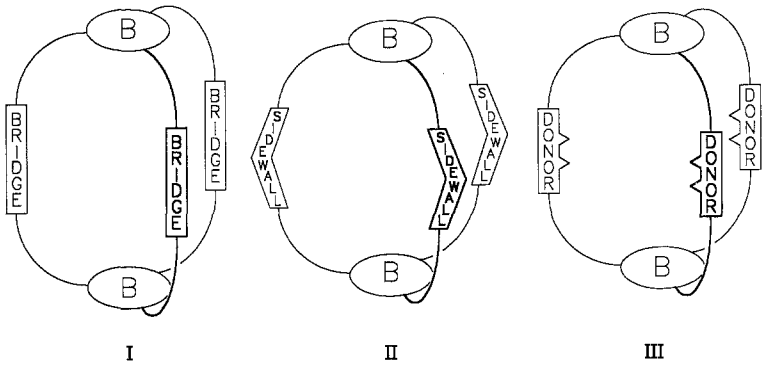


Fig. 20. Scheme of macrobicyclic cavity types [93, 94].

can be bridged appropriately (Figure 20). The first successful approach based on the structural principle of a common cryptand (cf. **40, 41** in Figure 13), i.e. two trivalent nitrogen atoms were brought in bridgehead positions. Bridging of these atoms by rigid spacers (cf. II in Figure 20) such as *o*-terphenylene yielded a cavity molecule **59** with a lenticular shape (Figure 21) [95].

Host molecule **60** shown in Figure 21, contains one triphenylamine and one triphenylmethane bridgehead unit [96]. These are bridged by three flexible chains which makes adaptation of the host molecule possible. Nevertheless, **60** has a permanent cavity suitable for the selective inclusion of disk-shaped naphthalenediols.

Replacement of the triphenylamine bridgehead unit by another triphenylmethane building block yielded host molecules **61** and **62** (Figure 21) [97]. They are topological isomers (*out/out*, *out/in*). A typical behaviour of the *out/out* isomer **61** is the inclusion of the highly lipophilic spherical adamatane molecule, which contrasts with the inclusion behaviour of **60**. The *out/in* isomer **62** also failed to enclose adamantane [97].

Host molecules with different cavity dimensions were designed using a symmetrically trisubstituted benzene nucleus as bridgehead unit [98–100]. Examples of molecules are **63** and **64** in Figure 21. The cavity of **63** is ideally suited for the molecular inclusion – and solubilization (in acidic water) – of large discoid lipophilic guest molecules like triphenylene and pyrene [98, 99].

The macrocyclic host molecule **64** containing three azobenzene units functions in a responsive manner [100]. It alters the cavity size and shape upon irradiation. All four possible *E/Z*-isomers of the molecule have been isolated.

3.5. HOST CAVITIES WITH DONOR OUTFIT AND FUNCTIONAL GROUPS

At a first glance, and if topological considerations are well to the fore, there seems to be no vast difference between a cavity with inside donor atoms or functional groups and one without (Figure 20). However, the fact is that there is really a vast difference. Generally it is difficult to force polar donor sites or functional groups inside the cavity into converging positions [21]. This holds for synthetic and conformational aspects as well.

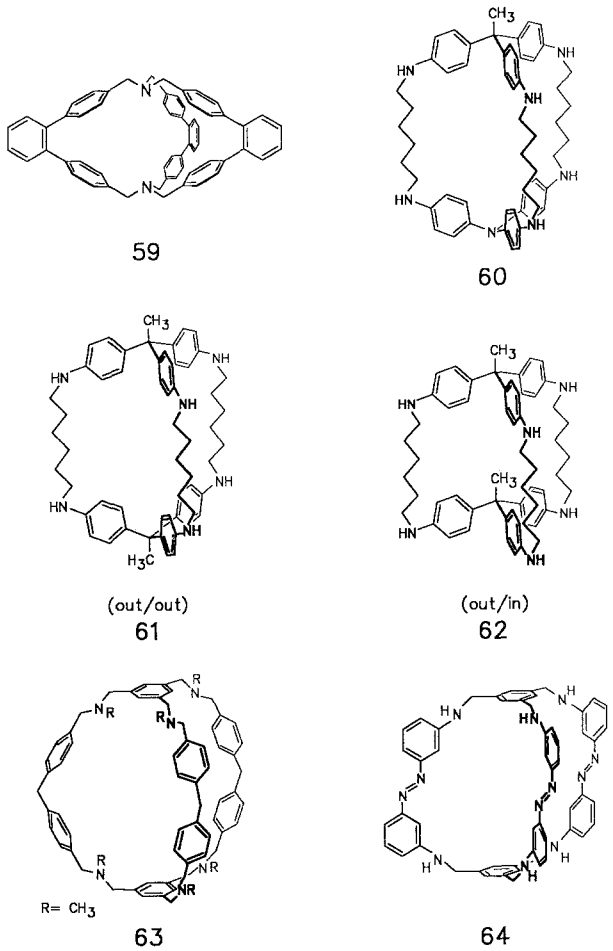
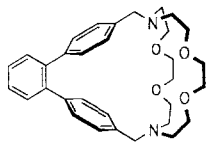


Fig. 21. Macrobicyclic hosts to include lipophilic guest molecules [95–100].

Consequently, we chose the easiest route and started rather trivially, i.e. we synthesized the rigid cryptands **65** and **66** (Figure 22) [95]. These cryptand type molecules combine typical oligoether segments of the cation complexing spacers such as in the cavity molecule **59** (cf. Figure 21). Hence, they are special cases of cryptands depending on the number of oligoether and aromatic segments. Due to the presence of a diaza-18-crown-6 moiety, **65** complexes Na^+ ions with high selectivity [95].

Whereas compounds **65** and **66** contain the usual nitrogen bridgeheads, hosts **67** and **68** (Figure 22) [101] with aromatic bridgehead units are close to the cavity molecules **63** and **64** (Figure 21). Nevertheless, because of the oligoether segments in **67** and **68**, they complex cations rather than uncharged organic molecules [101].

Topologically, the cavity molecules **69** and **70** (Figure 22) [102–104] are also cryptands. They have the same nitrogen or trisubstituted benzene bridgeheads as before. However, what makes these structures so complex is that three complete



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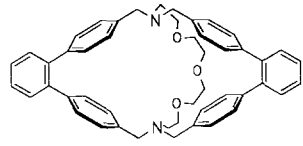

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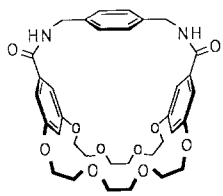

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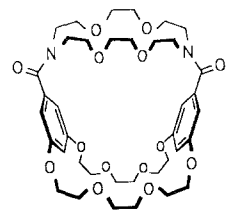

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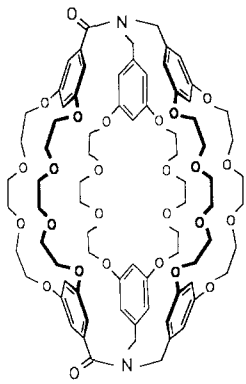

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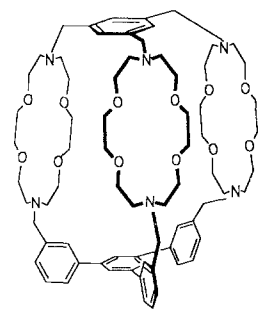


70

Fig. 22. Macropolycyclic hosts incorporating crown units (polyether segments) [95, 101–104].

crown rings form the bridges. As expected, the macropolycyclic tris-crown hosts **69** and **70** complex alkali metal ions [102–104]. Interestingly, host **70** was also found to complex oligophenolic molecules [104].

How about the problem with the functionalized cavities? Could it be solved? Well, we crossed that bridge when we came to it, as is obvious from Figures 23 and 24, which show logical series of functionalized host cavities **71** – **74** and **77** – **80** [93, 94, 105]. They are derived from typical catechol or bipyridine building blocks and different spacer (bridgehead) elements, thus leading to cavities with various functions, sizes, and shapes.

Most of these host cavities efficiently include cations and phenolic hosts, but some provide amazing complexation properties. Examples of such complexes (**75**, **76**, **81**, and **82**) are illustrated in Figures 23 and 24. For instance, the macrobi-

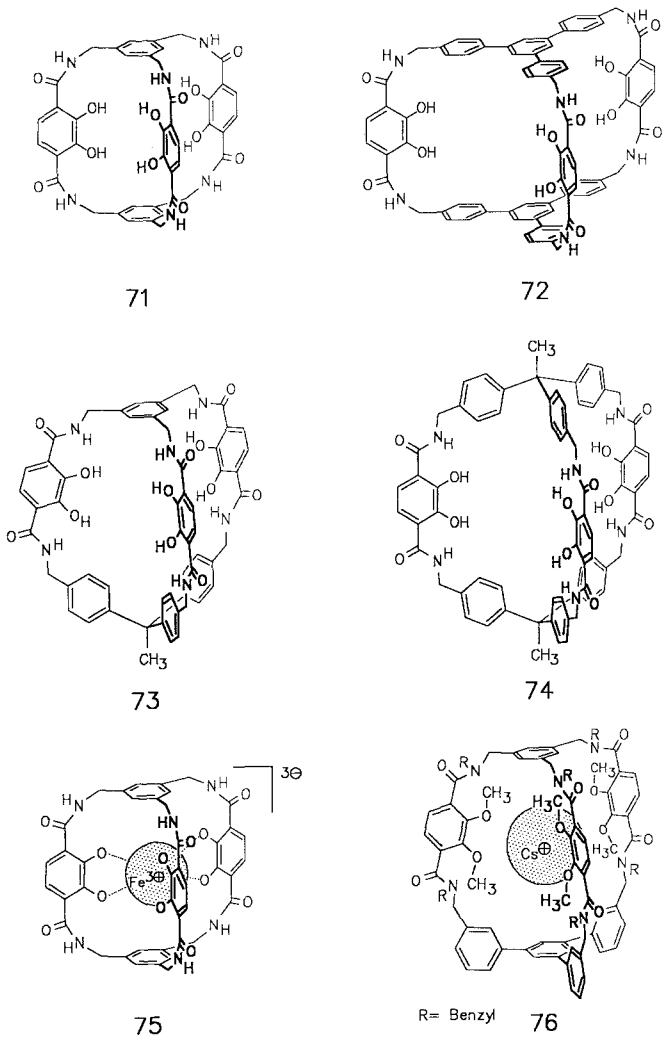


Fig. 23. Macrobicyclic tris-catechol hosts and typical complexes [93, 94, 105–107,110].

cyclic tris-catechol host **71** complexes Fe^{3+} as in **75** (Figure 23) [106] with $K_s \approx 10^{59}\,l\,mol^{-1}$ [107]! It is thus an even stronger Fe^{3+} binder than the natural siderophore enterobactin ($K_s \approx 10^{52}\,l\,mol^{-1}$) [105].

Another complex of high stability, **81** (Figure 24), is formed between tris-bipyridine host **77** and Ru^{2+} ions [108]. This ruthenium complex exhibits double the lifetime of the excited triplet state in comparison with $Ru(bipy)_3^{2+}$ but at the same time has a higher photostability, by a factor of 10^4 [109]. For that reason, the present Ru^{2+} complex of **77** is very promising in photophysics [94].

The analogous hexamethoxy host molecule, such as in **76** (Figure 23), forms a selective inclusion complex with Cs^+ ions which is very interesting in analytical

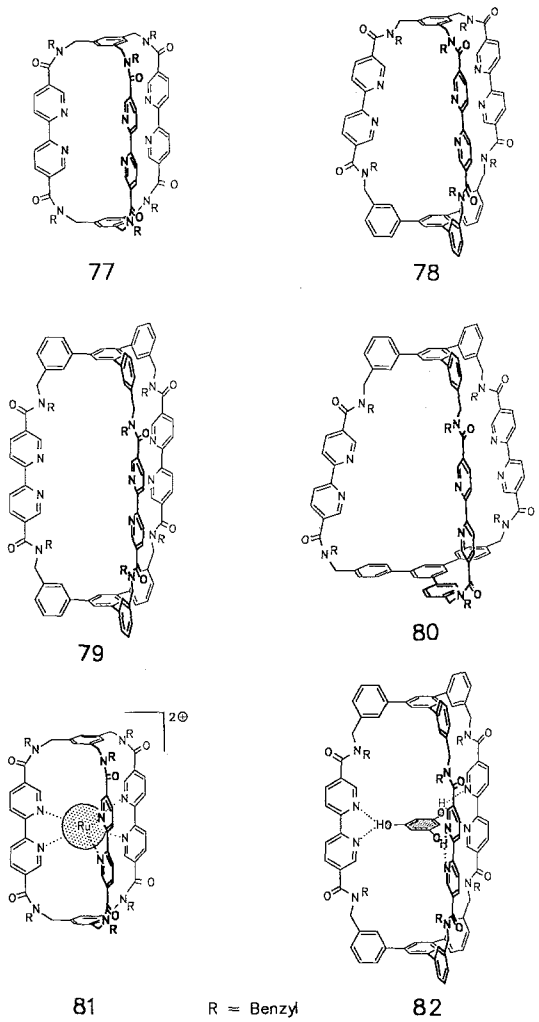


Fig. 24. Macrobicyclic tris-bipyridine hosts and typical complexes [93, 94, 108, 109, 111].

and radio medicinal chemistry [110]. Moreover, the tris-bipyridine host **79** (Figure 24) encloses phloroglucinol with an association constant K_{ass} of more than $10^4\,l\,mol^{-1}$ [111]. A proposed structure of this complex (**82**), where hydrogen bonds are involved, is shown in Figure 24.

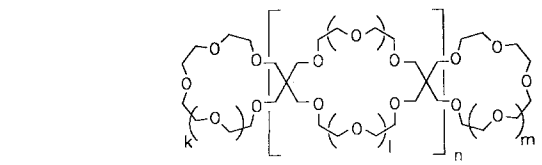
The modular synthetic strategy (cf. Figure 20) used for the synthesis of these macrobicyclic hosts allows broad structural variation [93, 94]. We are currently following this line in order to make available new, selective and strongly complexing host cavities with various sizes, shapes, polarities, and endo-functions [112] – similar to Pedersen, who had demonstrated it in outline with his original crown compounds.

4. Weber Group Research at Bonn University

4.1. THE MULTI-LOOP APPROACH: COMPLEXATION OF CATION ARRANGEMENTS

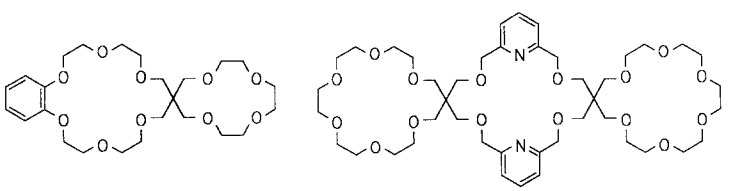
At the beginning in 1978, the Weber research group was only two persons, including Weber himself. Accordingly it was difficult to study crown chemistry over a wide range and one had to decide on one or two particular topics. It appeared very promising to develop ligands which enable a close association of more than one alkali or alkaline earth metal ion. Hence we settled on this topic.

The novel host design which was considered first features a spiro-linked assembly of two to four individual macrorings differing in ring size, rigidity, and donor characteristics [113]. Typical compound examples are specified in Figure 25 (**83**–**85**). Due to their particular topology, these new hosts were dubbed 'multi-loop



83

k = 0–4; l = 1, 2
m = 0–2; n = 0, 1, 2



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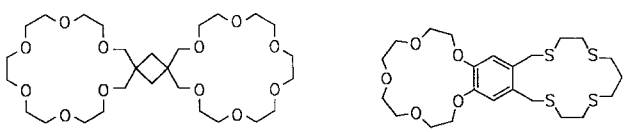

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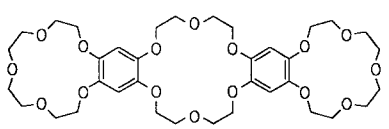


88

Fig. 25. Multi-loop crown compounds for complexing cation arrangements [113–115].

crowns' [114]. The synthesis of these species is based on the pentaerythritol unit providing the spiro linkage and involves skillful use of blocking/deblocking procedures and high-dilution techniques. Later we, extended our methodology to cyclobutane dispiro systems, as in crown compound **86** (Figure 25) [114] and, more recently, the spiro linkage was replaced by an aromatic unit to yield another new multi-loop crown topology, such as in compounds **87** and **88** (Figure 25) [115].

As expected, these new ligands are efficient multisite receptors for cations [113–115]. They were shown to be generally suitable hosts for the common incorporation of identical or different metal ions (to give homo- or heteronuclear complexes, respectively), corresponding to the specific binding characterization of the individual coordination compartments combined in the ligand skeleton. However, cooperativity and allosteric behaviour is also observed in the complexation properties, which originates from an interaction of adjacent binding sites. Thermodynamic and kinetic data of the complexation from ^{23}Na NMR studies are available [116] and the transport property of Pr^{3+} across a phosphatidylcholine vesicle membrane mediated by a diloop crown (**83**; $k = 4, m = 0, n = 0$) is reported in Ref. 117. We were also successful in isolating a great many crystalline multinuclear cation complexes [113–115].

In one case of a metal ion complex, we dispose of a crystal structure (Figure 26) which shows several interesting points [118]. Each loop of the crown compound (diloop) contains one Li^+, thus exhibiting a biloculi receptor behaviour. There is also one water molecule in each loop, the function of which is to fill the host cavity (19-membered crown ring) which is definitely too large for Li^+. The included water molecule is coordinated to the Li^+ and to two of the ether oxygens. A second coordinated water molecule lies outside the ligand cavity.

4.2. RINGS AND CHAINS: THE DONOR SIDE ARM APPROACH

Next we attempted to enhance the complexation strength of crown compounds by using something other than the cryptand strategy which causes unfavourable kinetics [119]. A possible solution considered was to use a crown with secondary

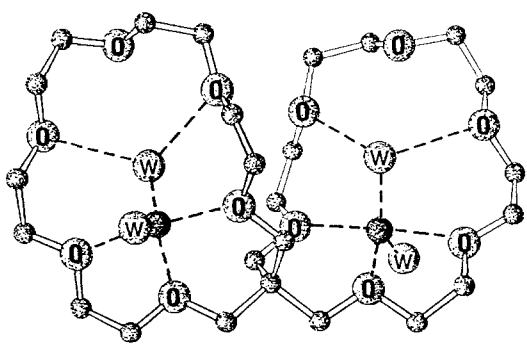


Fig. 26. Perspective view of the dinuclear hydrated LiI complex of diloop crown compound **83** ($k = 2, m = 2, n = 0$): simultaneous complexation of a metal ion and water (W). Neither iodide anions nor hydrogen atoms are included in the figure [118].

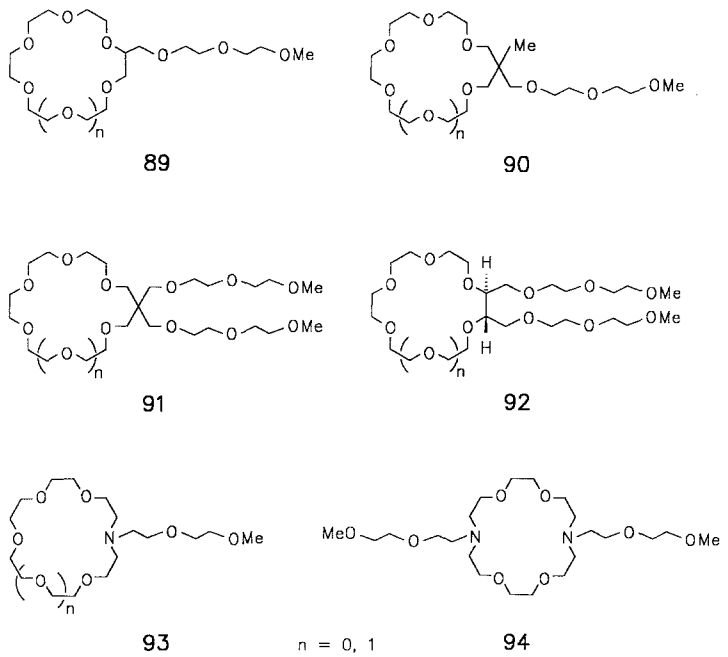


Fig. 27. Crown compounds with donor side arms: lariat ethers [122, 123].

donor groups bound to the macroring by flexible side arms, later termed 'lariat compounds' [120]. It happened: compounds of this type were synthesized in Bonn and almost simultaneously by the group led by G. Gokel [121]. Apparently (as for the pyridino crowns, see Section 2.2) two groups had the same idea at nearly the same time.

Compound examples (**89–94**) typical of our lariat design are illustrated in Figure 27 [122, 123]. They involve differently sized crown rings with one or two lariat arms attached to carbon or nitrogen pivot atoms. These compounds are relatively strong binders of cations (e.g. Na^+ as determined by ^{23}Na NMR spectroscopy) [122] and show efficiency in solid-to-liquid and liquid-to-liquid phase transfer of cations [123]. Since that early work, a great number of analogous lariat compounds have been synthesized and studied globally [120, 121], mostly for the purpose of the solvent extraction of cations [124].

4.3. PARTLY CROWN, PARTLY SURFACTANT: CROWN COMPOUNDS WITH LIPOPHILIC SIDE ARMS

In another approach for enhancement of the cation extraction and transport properties of cations, alkyl side arms have been appended to crown rings in order to provide additional lipophilicity. This led to highly lipophilic compounds such as **95–100** (Figure 28) [122–125]. They show quite remarkable solid-to-liquid and liquid-to-liquid phase transfer properties of cations as well as cation transport across a liquid model membrane [123, 125]. Crystalline complexes with alkali and alkaline earth cations were also isolated [125, 126].

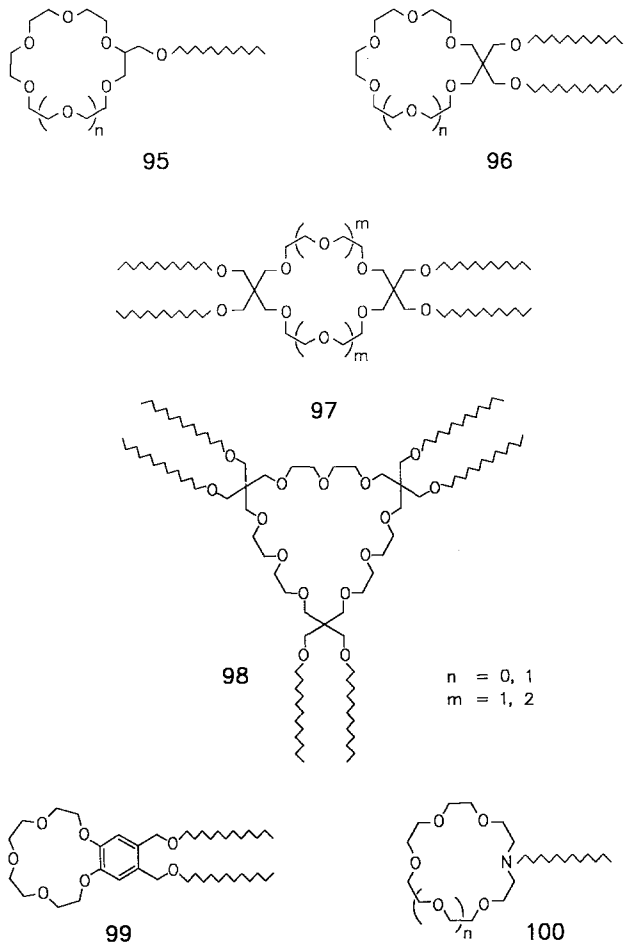


Fig. 28. Crown compounds with lipophilic side arms [125].

However, due to the particular structure (combination of a hydrophilic crown unit with a distinct lipophilic constituent) some of the molecules in Figure 28 behave as a typical surfactant, showing micelle formation and a cloud point [125].

In the solid state, the cation complex between **96** ($n = 0$) and Na^+, which was studied by X-ray crystallography (Figure 29) [126], reveals interesting parallels to certain membrane-forming lipids, including an analogous helical kink in one of the alkyl chains and the double layer structure characteristic of lipid crystals. Thus the surfactant type crown ethers are suitable as model compounds for biogenic lipid molecules and are suggested for use as ion-selective membrane carriers [127]. Aza compound **100** was a model to develop the 'annilides' [128].

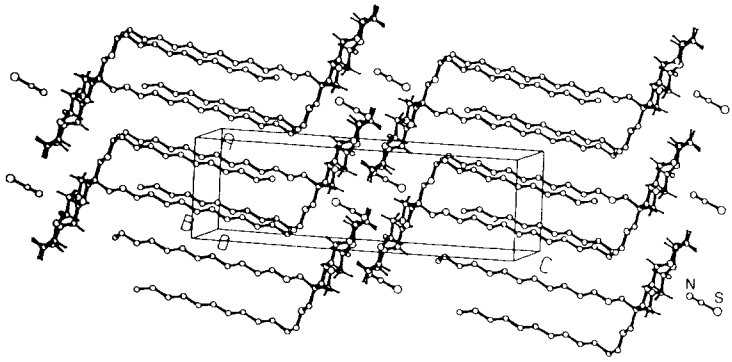


Fig. 29. Molecular packing in the crystal of the NaSCN complex of surfactant-type crown compound **96** ($n = 0$, Fig. 28) showing the double layer formation and the helical kink [126].

4.4. DISCOID AND SPHERICAL OLIGO-CROWNS: NEW TOPOLOGIES OF SURFACTANT MOLECULES

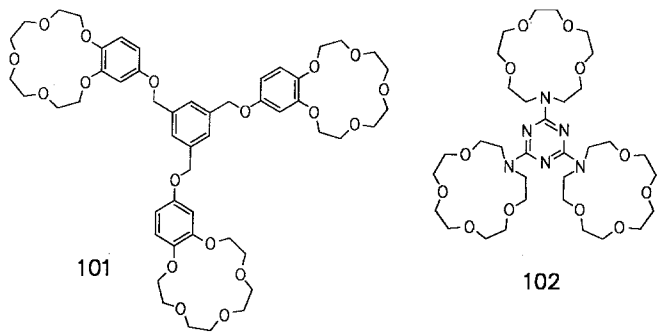
The type of compounds (**101–103**) exemplified in Figure 30 involved perhaps the greatest surprise to use. Originally, these molecules were intended as multisite cation receptors (cf. multiloop structures, Section 4.1.) having a new spherical topology. However, interest in this class of substances developed in a different way. Although the type of compounds specified in Figure 30 does not consist of a lipophilic and a hydrophilic part as in a typical surfactant structure, the substances behave in a similar manner [129]. Instead, these molecules are characteristic of a variable number of crown subunits (three to six) attached to a central aromatic or heteroaromatic core using different linkage elements (cf. Figure 30).

The compounds are highly soluble in water, wet a contiguous glass wall, and show foaming ability. The surfactant character is illustrated even more clearly by the occurrence of cloud points in water (between 24 and 85°C, 10^{-3} M solution), which are directly related to the molecular structure (the cloud point decreases with increasing conformational flexibility of the molecular framework and *vice versa*). Critical concentrations for micelle formation are in the range of 10^{-4} with aggregation numbers of about 50–80 [129].

Thus, the oligotopic crown compounds of type **101–103** are surfactants having a novel construction principle [130]. The compounds may also be understood as structural forerunners of the now rather important discoid liquid crystal forming substances. [131].

4.5. HIGHLY BENZO-CONDENSED CROWN VERSIONS

Although dibenzo-18-crown-6 (**12**; Figure 3) was the initial crown ether discovered by Pedersen [1, 2], analogous crown compounds with a higher number of aromatic rings and with benzo condensations in different positions remained practically unexplored [3, 132] until we set to work on it. As we saw it, such compounds combine several properties which show promise for selective cation complexation, including steric shielding, molecular rigidity, and reduced donor ability. Thus, to fill



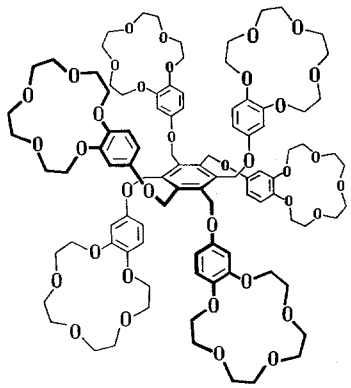


Fig. 30. Discoid and spherical multiloop crowns with surfactant behaviour [129].

this gap, we synthesized hitherto absent members of the series of 18-crown-6 rings with oligo-benzo condensation [133]. Characteristic examples of compounds are specified in Figure 31.

In fact, the oligo-benzo crowns responded with remarkable selectivity to cations, when used in liquid membrane electrodes [133]. In calorimetric titration studies, complexation of protons (in acetonitrile) correlates well with the number of benzo units present in these compounds (complexation decreases with increasing number of

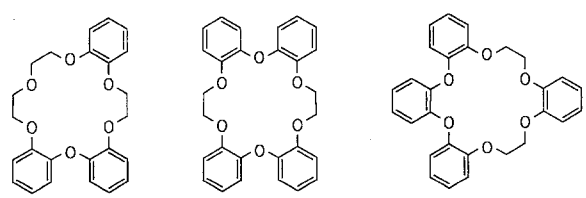


Fig. 31. Highly benzo-condensed 18-crown-6 derivatives [133].

benzo units) [134]. Also, some of these macrorings (e.g. **106**) yield crystalline inclusion complexes with water and small organic molecules, as a result of their rigid cavity structure [133].

4.6. DESIGN OF HETEROAROMATIC AND CAVITAND-TYPE CROWN RECEPTORS FOR UNCHARGED ORGANIC MOLECULES

There is no reasonable explanation why the discovery by Charles Pedersen at the beginning of the seventies that crown ethers are capable of complexing uncharged organic molecules [74] (cf. Section 3.4.) remained so long on the shelf before stimulating people. Actually, up to the end of the seventies, complexes between crown compounds and uncharged organic molecules were very rare; mostly such studies related to complexes of 18-crown-6 and they were rather accidental discoveries [80, 81]. Later, crystalline complexes of crown compounds with CH– and NH–acidic uncharged guest molecules became more and more numerous, but the formation of analogous complexes with OH–acidic guests, such as alcohols, remained unsuccessful over a long period [135].

However, the answer followed quickly when we considered ligands with one or two pyridino units and a certain number of aromatic groups gathered in a macroring, of which compounds **107–112** (Figure 32) are typical [136–141]. These macrorings may be seen as descendants of compound **31** (X = N, Figure 9), which also shows crystalline complex formation with uncharged organic molecules (mainly of dipolar aprotic nature) [142], but compounds **107–112** and their analogs are more efficient. They form crystalline complexes with organic guests in a broad range, including alcohols [135–141]. Nevertheless, crystalline complex formation is highly selective for each macroring, depending on the structural parameters of host and guest.

For instance, host compound **107** (R = H) yields a stable 1 : 2 stoichiometric inclusion compound with methanol (hydrated) [136], whereas **107** ($R = CMe_3$) which is substituted by a voluminous *t*-butyl group, cannot [137]. The latter macrocycle, however, binds 2-propanol highly selectively.

When complexing methanol by **107** (R = H), the conformation of the host molecule changes significantly from a closed to an open structure, as evidenced by crystal structure analysis [143]. A unique host–guest order is found for the methanol complex of **107** (R = H) involving an almost linear O—H···N host–guest hydrogen bond and an intra-cavity oriented methyl group of the guest, as shown in Figure 33a [143]. The high selectivity of **107** (R = H) for small unbranched alcohols is now evident for spatial reasons. This is probably the first example of neutral guest complexation via hydrogen bonding inside a host cavity niche [88, 135].

Replacement of the benzo rings by naphtho units, as in **110**, gives rise to a molecular conformation with two deep clefts. They are potential sites for locating guest molecules. Figure 33b illustrates the crystal structure of the 1 : 1 dioxane complex of **110** [140].

Another unique property occurring in this class of compounds is face differentiation with reference to the host macroring and uncharged guest molecules. This is obvious when comparing Figure 33c with Figure 33d, which show the crystal structures of the complexes of macroring **111** with MeCN (1 : 2) and $MeNO_2$ (1 : 1), respectively [144, 145].

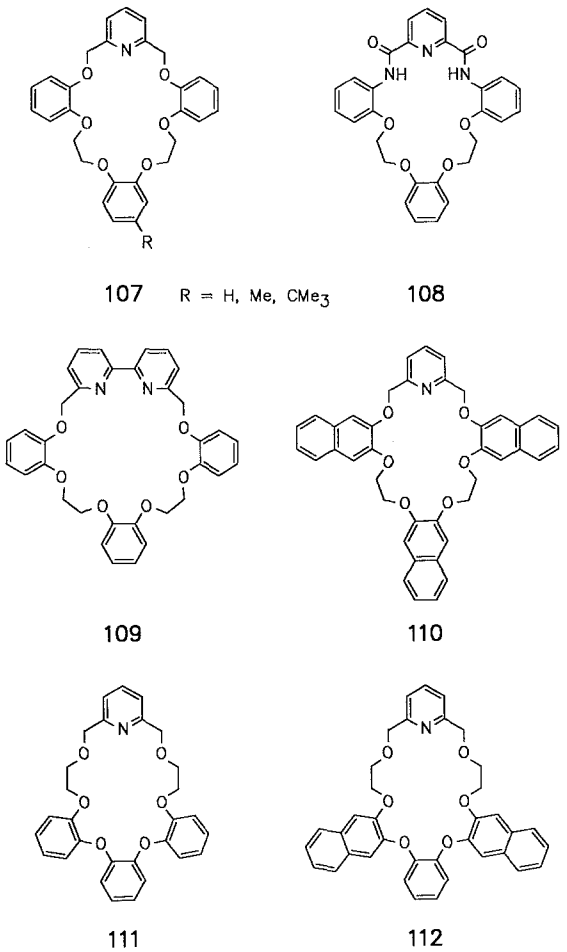


Fig. 32. Heteroaromatic crown hosts which form uncharged molecule complexes [136–141].

The net conformational geometry of **111** is the same in both complexes, providing the host molecules with two concave faces (A and B in Figure 33a and 33b). One (A) has the rough appearance of an ice-cream cone and offers a relatively deep and narrow cavity, the other (B) is similar to a book-rest with a relatively wide and low shielded hollow. For steric reasons, the MeCN and $MeNO_2$ guests, which are rod-shaped and Y-shaped molecules, respectively, are correspondingly distributed between A and B in the present complexes (Figures 33a and 33b) [144, 145]. Besides the spatial relations, motifs of polarity and hydrogen bond complementarity between the different host faces and the two guests are also evident.

There are many more uncharged guest complexes and free molecules of this host class which have had their structures solved, involving macrocycles with different aromatic and heteroaromatic building blocks, donor sites, ring sizes, and rigidity, as well as guest molecules of different sizes, shapes, and polarity [146–151]. Thus, the complexation chemistry of semi-rigid macrocyclic pyridino-, bipyridino-, and

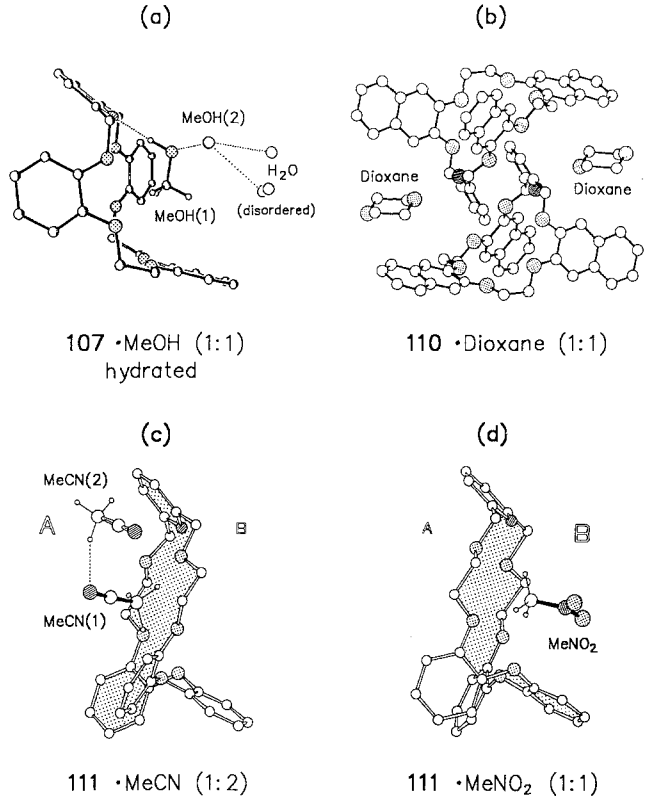


Fig. 33. Crystal structures of typical pyridino crown complexes with uncharged organic molecules (O atoms dotted, N atoms hatched) [140, 143–145].

phenanthrolino-containing hosts with uncharged organic guests is highly developed at the present time [135].

Recent investigations in our laboratory are keyed to the development of macrocyclic receptors which have a defined cavity and specific inward-facing functional groups, e.g. strong proton donor and acceptor sites. Typical examples are the macrocycles **113** and **114** (Figure 34a) [152].

Macroring **113** forms a unique 1 : 1 inclusion compound with DMF, the structure of which is shown in Figure 34b [152]. The guest molecules of DMF (disordered) are in the center of the macroring, aligned with an intra-host channel. Macrocycle **114** is promising as a selective extractant (solvent–solvent) for small alkaline earth metal ions [153].

4.7. MACRORING VERSUS LATTICE CAVITY: HOST–GUEST CHEMISTRY IN THE SOLID-STATE, INCLUDING CLATHRATES, COORDINATOCLATHRATES, AND CRYSTALLINE COMPLEXES

Since the middle of the eighties, research in our group shifted increasingly from the crown cation complexes and molecular inclusion compounds to the lattice-type

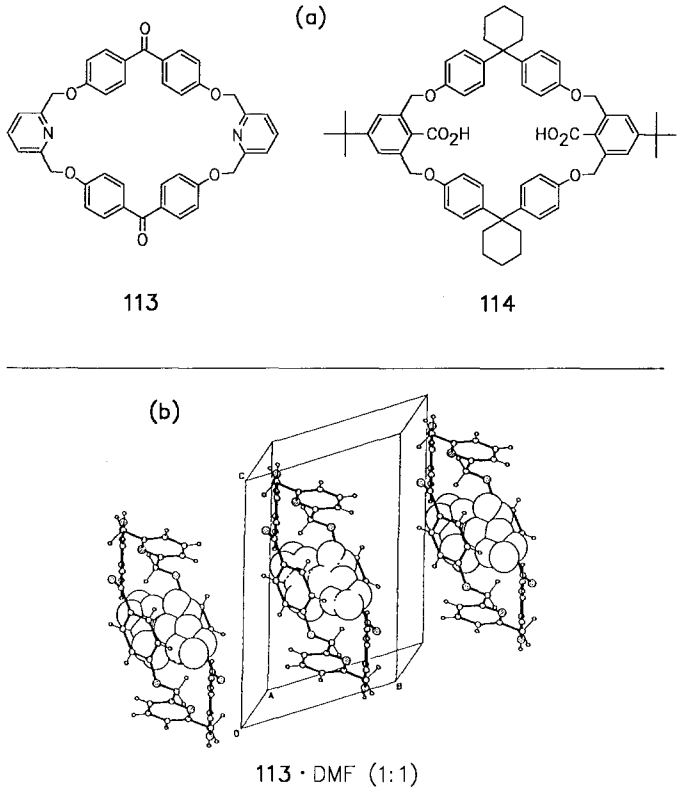


Fig. 34. Cavitand-type hosts (a) and crystal structure of an inclusion compound (b) [152].

inclusions (clathrates) [154, 155] and supramolecular crystals [156]. They are now the main topics of our research. To steer the discussion to the point, Pedersen never worked with host lattices and clathrate compounds. Actually, the existence of such species was recorded long before Pedersen [157]. Nevertheless, by his promotion of the general inclusion idea, he also stimulated, albeit unintentionally, these particular fields of host–guest chemistry, giving them a tremendous impulse in the last few years [45, 154–159].

The attraction of the lattice (clathrate) approach for forming inclusion compounds lies in the fact that you can use small host molecules for cavity formation and thus avoid a troublesome synthesis of macrocyclic host cavities (multimolecular vs. monomolecular cavity formation, cf. Figure 35) [160]. On the other hand, the small clathrate hosts were subject to a high degree of randomness, and only very recently have some helpful design principles for clathrate hosts been developed [161].

Possibly the most general ones which came from our group are obvious from Figure 36 and we may state the following [162]: a clathrate host molecule which will crystallize in such a form as to leave hollow spaces in the crystal lattice for guest inclusion should be: (1) bulky in constitution to cause the lattice holes; (2) it should have a rigid conformation to maintain the cavity structure; and also (3) one

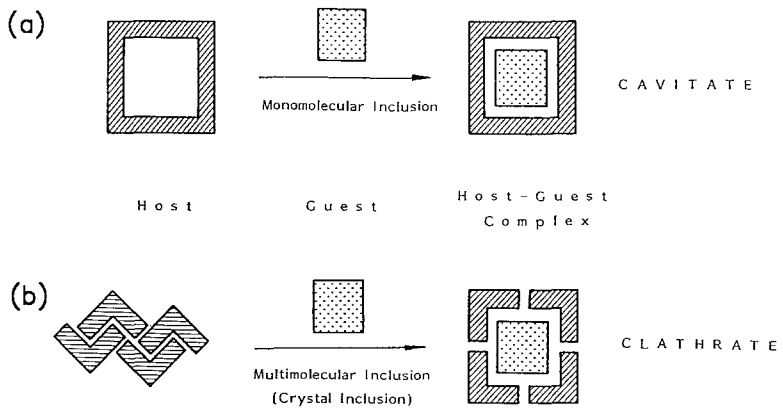


Fig. 35. Strategies of inclusion formation [160].

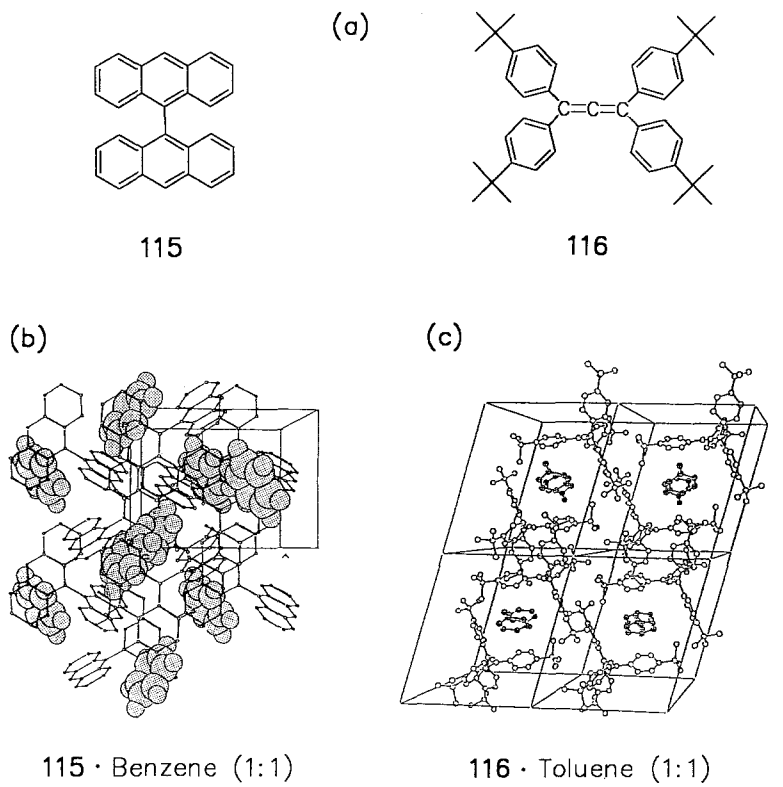


Fig. 36. Apolar lattice hosts (a) and crystal structures of corresponding inclusion compounds (b, c) [163, 164].

should aim for a balanced symmetric overall shape of the molecule, which will help in the stabilization of the crystal lattice.

Compounds **115** and **116** (Figure 36a) are representative examples of host molecules which meet these principles [163–165]. In terms of their shape they belong to the scissor-type constitutions [166, 167]. Other examples relate to a molecular roof [167] or are based on a rigid, small ring [168, 169].

Crystalline inclusion structures involving the host compounds **115** and **116** and benzene or toluene guest molecules, respectively, are illustrated in Figures 36b and 36c [163, 164]. They underline the presence of spacers, arene units and bulky groups arranged in a geometric pattern as being important in creating a porous host lattice with cages (Figure 36b) or channels (Figure 36c) that makes hydrocarbon guest enclosure possible [162]. The inclusion formation is driven by the dense crystal packing [170] which is obtained when guest molecules fill the hollow space of the host lattice rather than by specific molecular interactions [156].

However, inclusion is believed not only to be the result of sterical properties but also of molecular polarity relations where oriented dipole interactions or hydrogen–bonding between host and guest are contributing factors [155, 156]. Clearly, the use of the properties of polar functions or groups which may allow hydrogen bonding would substantially enlarge the scope of crystalline hosts and guests. This prompted us to develop the so-called principle of 'coordination-assisted clathrate formation' [160, 167].

As suggested by the term, a coordinatively assisted clathrate, or 'coordinatoclathrate', involves a hybrid between a complex and a clathrate (Figure 37a) [160, 167]. Thus, coordinatoclathrates combine attributes of coordinative complexes and of lattice dependent clathrates, and this is the reason that they permit a high degree of selectivity in different directions, including chemoselectivity and constitutional selectivity, according to their origin (see Figure 37a). Consequently, a corresponding coordinatoclathrate host (Figure 37b) consists of two components: (1) a bulky basis skeleton that makes available lattice cavities typical of a clathrate (see above); and (2) appended functional groups (sensor groups) that manage the coordination to the included guest substrate [160, 167].

However, the realization of this idea is not an easy task since functional groups are mostly supplied with co-existing proton donor *and* proton acceptor sites, such as in carboxylic acids, amides, or alcohols. They tend to dimerize or oligomerize or influence one another, rather than to complex with a secondary component [160, 162].

We consider two possible ways out of this problem. One is obvious from the scheme given in Figure 38a [160, 166]. It involves the application of a steric barrier for suppression of the functional group contact between hosts in a localized or in a more integral sense. Yet these functions are available to complementary groups of sterically less demanding (smaller) guest molecules that are able to bridge the gap and to fill space.

A typical host molecule that approaches this idea is simple 1,1′-binaphthyl-2, 2′-dicarboxylic acid (BNDA) (**117**, Fig 39a) with salient scissor-type shape (Fig. 39b) [171]. Recrystalization of BNDA (**117**) from different alcohols (such as MeOH, EtOH, 1-PrOH, 2-PrOH, *t*-BuOH etc.) results in the formation of well-developed channels of approximately 6–7 Å diameter with a stoichiometric number of solvent molecules inside the channel.

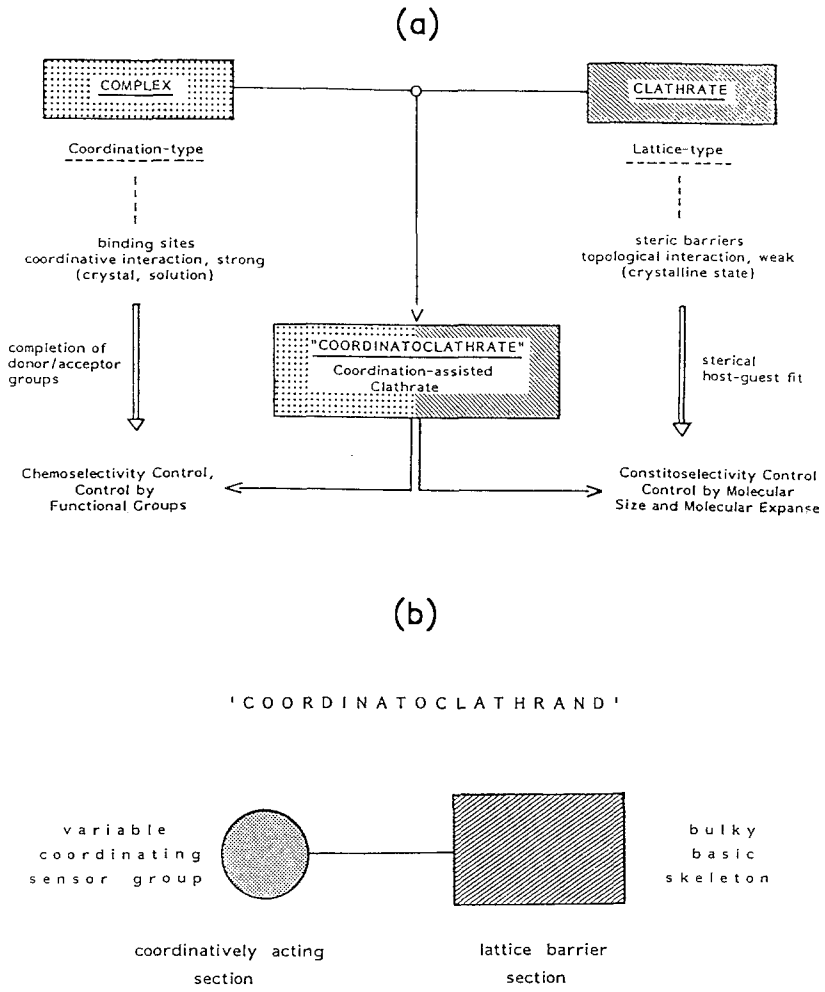


Fig. 37. Coordinatoclathrate concept (a) and abstracted structure of a coordinatoclathrate host (b) [160, 167].

Figure 39 (c–e) illustrates the facts for the inclusion compound of **117** with MeOH (1 : 2) [160, 167]. The channels (Figure 39c) have mainly an apolar surface that is interrupted periodically by hydrophilic narrowings consisting of the carboxylic groups (Figure 39d). The cross section of electron densities in this channel area (Figure 39e) clearly shows two facing carboxylic groups held at a noninteractive distance that follow closely the basic idea of Figure 38a, namely formation of a specific gap in the crystal lattice. Here are the sites at which the accommodated guest molecules (MeOH) contact the host.

This is more evident in Figure 39f, which shows a detail of the crystal structure of inclusion compound **117** · MeOH (1 : 2) [171]. Bridging of the gap is *via* two

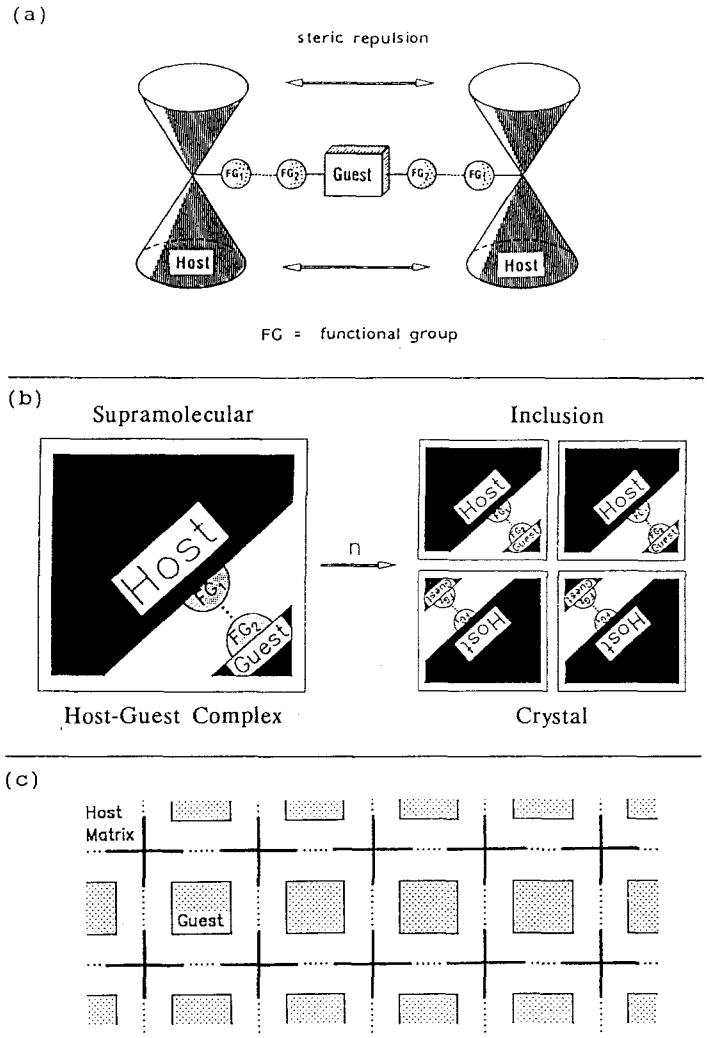


Fig. 38. Principles of crystalline inclusion (clathrate) formation [160, 162, 166].

molecules of methanol providing a set of complementary hydrogen bonds to the carboxylic groups. Thus, a 12-membered ring system of coupled hydrogen bonds is formed.

Alcohols other than MeOH, as demonstrated by crystal structures [171, 172], are involved in the same or in a similar binding pattern of hydrogen bridges with the BNDA host (e.g. a 10-membered ring) depending on spatial properties. Other carboxylic [168, 169, 173–175] or carbonamide hosts [174, 176], such as the roof-shaped compounds **118** [173, 174] and **119** [176] or the small-ring derived molecule **120** [175] behave correspondingly (cf. Figure 38a) and form either cyclic (Figure 40a, b) [174, 176] or helical (Figure 40c) [175] systems of hydrogen bonds between host and guest in their inclusion compounds [160, 162].

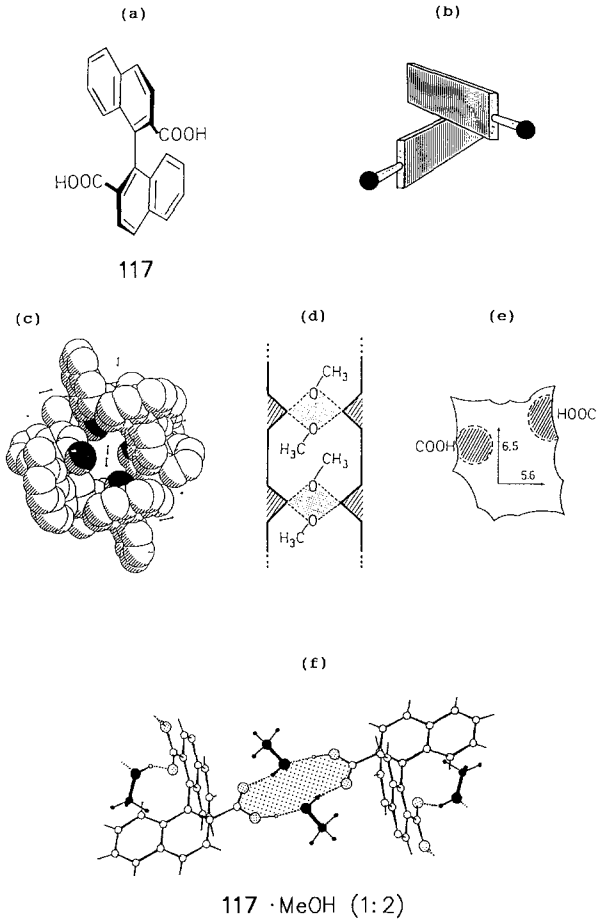


Fig. 39. Prototypical coordinatoclathrate host (a, b) and specification of its inclusion compound with MeOH (c–f) (H bonds shown as dotted lines) [160, 167, 171].

The second way to overcome the problem with complete dimerization of host functional groups interfering with the host–guest binding is to find a more convenient coordinative partner or complementary site than its own sort of functional group, i.e. to form a preferred host–guest complex, a supermolecule, which has an acceptable shape for crystallization (Figure 38b) [162]. An example is given in Figure 41a. The bulky diol host **121** shows high affinity for coordination with amines [177, 178]. When complexing the tertiary amine guest, a smooth surface of the supermolecule is obtained, which is suitable for crystallization.

Apart from using host functional groups for direct binding of polar guests acccording to the principles of Figures 38a and 38b, host functional group dimerization may be helpful for inclusion formation with apolar guests, as schematized in Figure 38c [161, 162] and illustrated in Figure 41b [179]. Dimerization of the carboxylic groups in the case of **117** results in a loose crystal packing. Consequently, a secondary component such as bromobenzene is required for filling the channel space, thus stabilizing the crystal lattice [179].

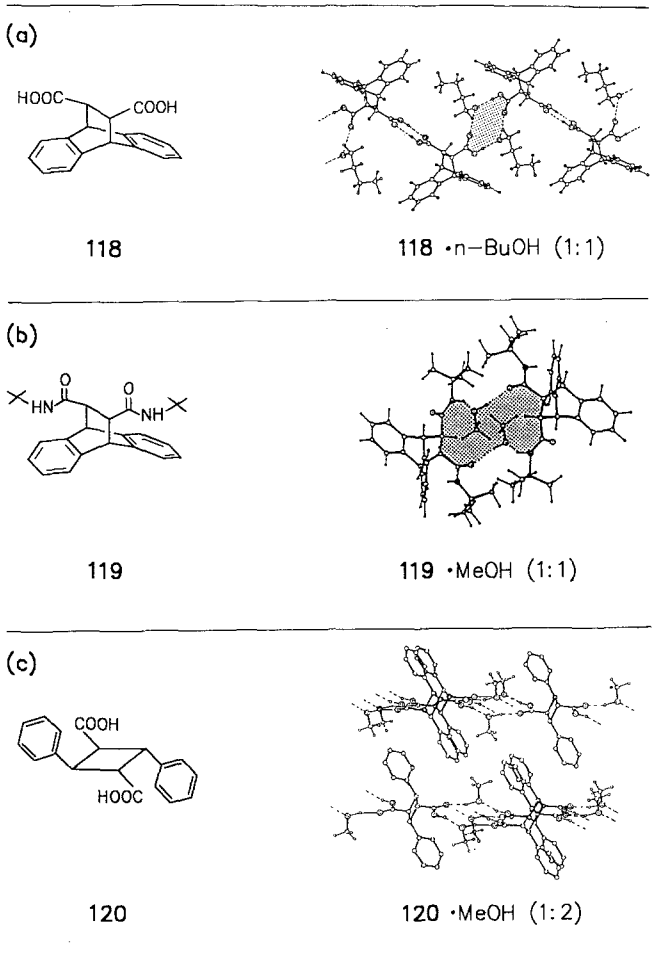


Fig. 40. Host molecules and inclusion structures (packing excerpts) showing the supramolecular binding pattern (H bonds shown as dotted lines; dotted regions indicate H-bonded rings) [174–176].

Similar factors are important in the formation of the inclusion compounds specified in Figure 42 [168, 169, 174, 176–181] and they also hold for the inclusion compounds of a large number of other hosts [182–193] developed by the design principles presented above [160, 162, 166].

This vast number of inclusion compounds were obtained by simple recrystallization of the host substance from the respective guest solvent or of host and guest from an inert solvent.

Guest competition experiments showed that each host compound provides a specific selectivity pattern of inclusion formation, dependent on the molecular parameters. Nevertheless, very simple host constitutions may give rise to unusually high guest selectivities. For example, triphenylmethanol forms a crystalline inclusion compound specifically with methanol from solution mixtures of alcohols [188]; triphenylsilanol does the same, but with ethanol [193]. Other hosts, such as **121** and

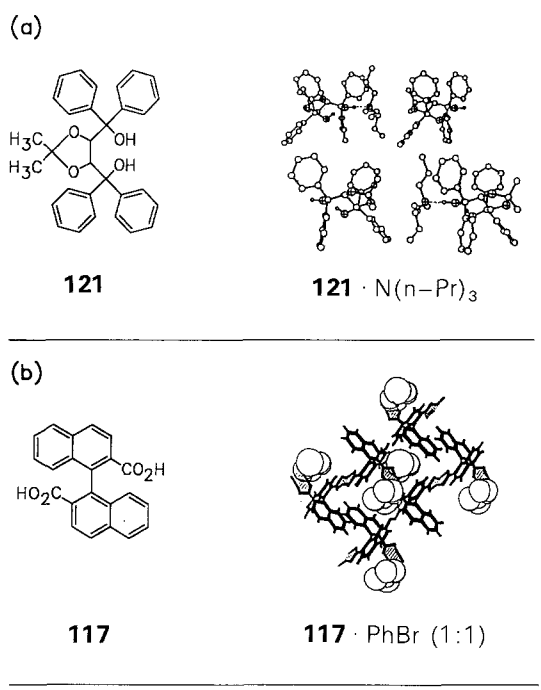


Fig. 41. Host molecules and inclusion structures (packing excerpts) typical of host–guest and host–host H bond interaction. In (a), H bonds are shown as dotted lines; the hatched regions in (b) indicate the H-bonded carboxylic group dimers [177, 179].

125–**127** are selective from solution for a particular type of amine [177, 178, 181, 194].

Moreover, the optically active hosts, which we have recently synthesized, are efficient in enantioselective inclusion of guests; e.g. optically active **125**, which can be derived easily from natural lactic acid, yields highly enantioselective inclusion compounds with chiral ketones [194]. It is also interesting to know that guests in the vapour state are also absorbed highly specifically from a vaporous solvent mixture by certain hosts to form the appropriate inclusion complexes [188, 190, 193, 194].

Thus, the simple compounds mentioned here are useful for sequestering chemical and stereochemical species in the liquid and vapour phase, comparable to the macrocyclic receptors initiated by Charles Pedersen. They are also promising in organic materials design [156, 162] and display some structural similarity, allowing them to mimic proteolytic enzymes [195].

5. Closing Remarks

It is clear that the scientific legacy of Charles J. Pedersen has deeply influenced our work on organic complexes and inclusion compounds from the beginning. We hope that this has been made evident by this paper, which has emphasized structural aspects.

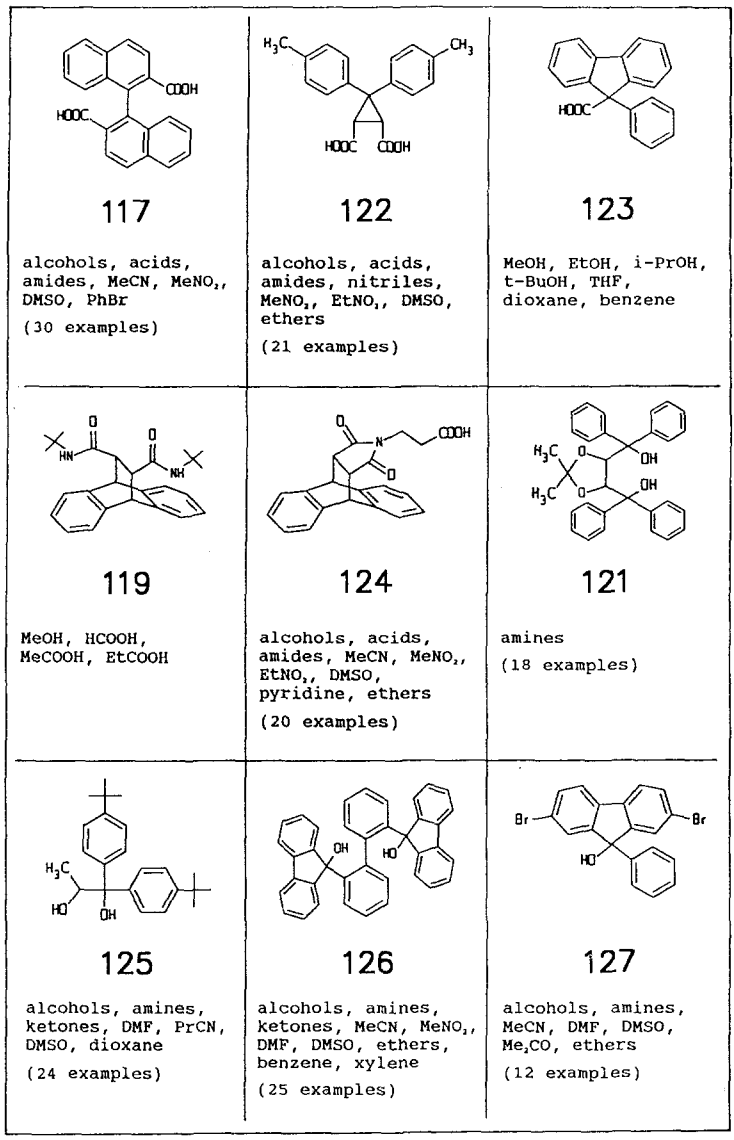


Fig. 42. Representative lattice host molecules and inclusion formation [168, 169, 174, 176–181].

Moreover, some general topics related to the host–guest and supramolecular fields with which we are involved, were also greatly stimulated. They include synthetic strategies, which were used before by other scientific groups, such as the 'high dilution reaction principle' [196, 197] which came to fruition, the so-called 'Cs-effect' [198, 199] which was developed for the purpose of strained macrorings, or certain repetitive synthetic approaches which lead to 'cascade' and nonskid-chain-like' molecular topologies, as specified in Figure 43 [79, 200]. Actually the latter synthetic strategy has opened up the recent design of three-dimensional,

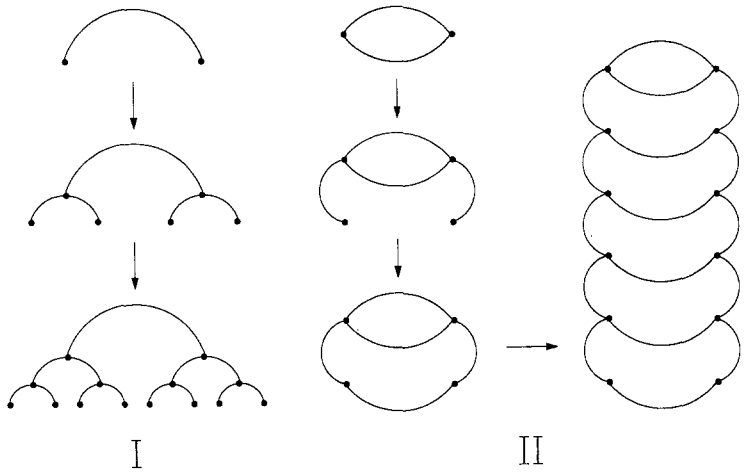


Fig. 43. Repetitive synthetic strategies for 'cascade' (I) and nonskid-chain-like (II) molecular topologies (I equals a second generation, II a fifth generation species) [200].

highly ordered oligomeric and polymeric compounds known as 'arborols' and 'star-burst dendrimers' [201].

Another, not synthetic, but no less important topic is nomenclature. The designation 'crown', coined and introduced by Pedersen [1], originally was only a nickname for a particular type of oligoether macrocycle. Naturally, the immense variety of crown-analogous compounds synthesized over the years called for a concise nomenclature. We have suggested useful nomenclature and notation systems [31, 202].

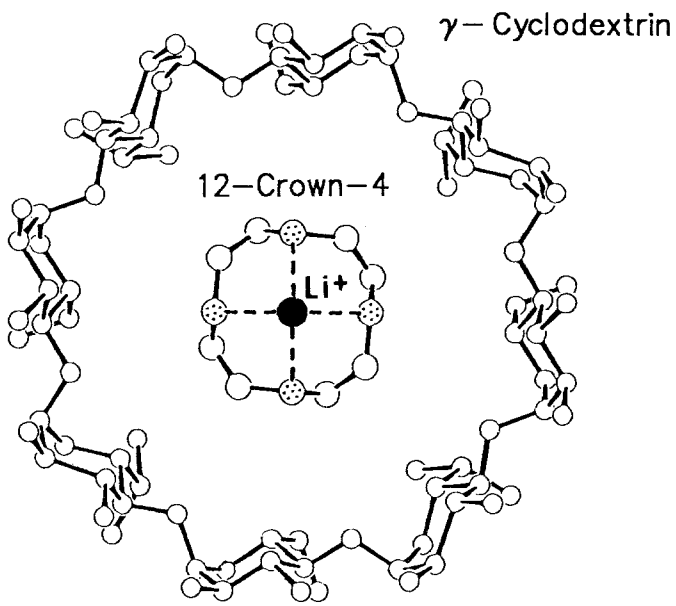


Fig. 44. 'Complexed crown': ternary complex between γ-cyclodextrin, 12-crown-4, and Li^+ [203, 204].

A final plum: perhaps the most appealing structure of crown chemistry is that of the supramolecular complex shown in Figure 44 [203, 204]. It involves Li^+, 12-crown-4 and γ-cyclodextrin nested in three spheres, i.e. a beautiful and symbolic combination of original Pedersen-crown and more recent supramolecular host–guest chemistry.

Unfortunately, it was not granted to both of us to meet Charles J. Pedersen himself in order to gain a lasting remembrance of his greatly esteemed personality. However, his brilliant ideas and scientific genius is still alive in his original papers and will certainly stimulate future topics of our research. Apart from that, the early work of D. J. Cram [205] and J.-M. Lehn [206], who won the 1987 Nobel Prize on chemistry together with C. J. Pedersen [1], was also fruitful in our research, to a degree.

Acknowledgements

We are deeply indebted to our coworkers, whose names appear in the references, for their tireless efforts. Their dedication has made possible the work described in this review. The authors thank the Deutsche Foirschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of their work. We are also grateful to M. Frank, R. Güther, D. Karbach, A. Lohner, C. Reutel, A. Schröder, and C. Seel for their help with the drawings of the formulae which appear here.

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