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First- and second-sphere coordination chemistry of alkali metal crown ether complexes

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Contents

Abstract

Crown ethers exhibit an extremely versatile range of interactions with alkali metal cations in the solid state that goes far beyond simplistic 'size fit' considerations. In this review the structural chemistry of first and second-sphere alkali metal cation complexes of the crown ethers is examined with an emphasis on the role played by hydrogen bonding interactions to

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counter anions and other co-ligands such as water. An examination of the vast diversity of alkali metal crown ether complexes and the strong propensity of the crown ethers to act as hydrogen bond acceptors suggests that hydrogen bonding plays a crucial role in determining overall structure.

Keywords: Crown ethers; Alkali metal cations; Hydrogen bonding

1. Introduction

Since their accidental discovery by Pedersen in 1967 [1,2] the crown ethers (Fig. 1) have proved to be enormously popular — and extremely useful — ligands (hosts) for a startling range of metal ions and neutral or ionic organic species [3]. Indeed, it seems as if they bind the majority of the elements of the periodic table. The chemistry of the crown ethers was first reviewed in 1974 by Izatt [4] and he (along with a growing legion of other workers [3]) has been kept busy by the enormous productivity of the field ever since [5,6]. One of the facets that has made crown ether chemistry so popular is the notion that these ligands may select the

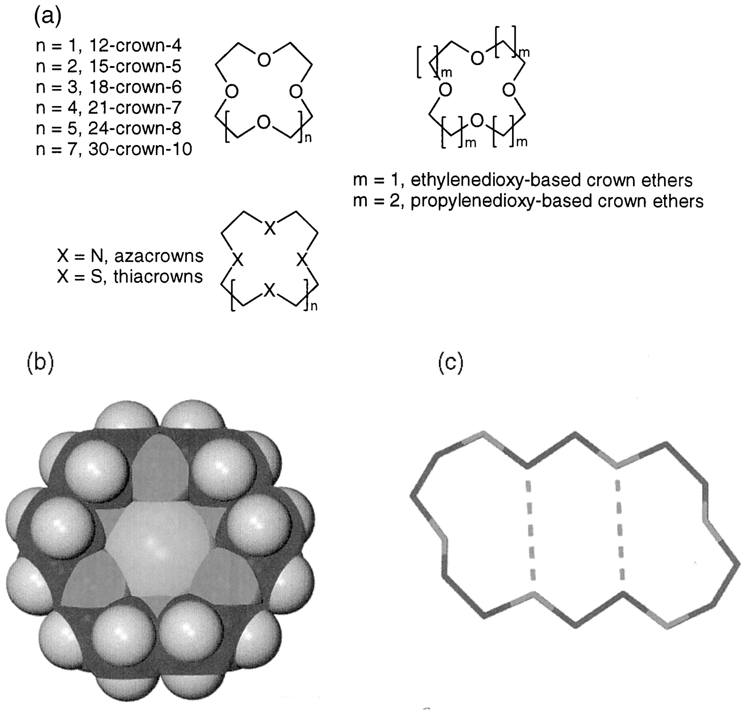


Fig. 1. (a) Generalised structure of the crown ethers, (b) Space filling view of unsolvated [K(18-crown-6)]$^+$, (c) X-ray crystal structure of uncomplexed 18-crown-6 showing intramolecular C–H···O hydrogen bonds.

metal cations that they 'choose' to bind on the basis of size fit within the interior of the macrocycle. Indeed it was suggested as early as 1971 that ratios of cation radius to crown ether internal van der Waals diameter of 0.75–0.90:1 were suitable for metal ion inclusion within the macrocycle [7]. This size fit argument as a basis for solution selectivity patterns has undergone much revision and addition, however, as crown ether chemistry has evolved, and factors such as preorganisation and complementarity [8], solvation and, significantly, chelate ring size [9] are now accepted to be the most significant factors involved in the solution selectivity of the crown ethers. Indeed the highly flexible crown ethers have proved to be capable of adapting themselves to a wide variety of coordination requirements and media. Their flexibility imparts some very interesting properties such as solubility in both aqueous and lipophilic solvents and rapid, reversible ion binding characteristics. On the Hansch lipophilicity scale (based on measurement of the octanol water partition coefficient), 18-crown-6 has a value of exactly zero, indicating a perfect balance between hydrophilicity and lipophilicity, a feature that is a result of the flexibility of the ligand enabling it to expose either hydrophilic ether oxygen atoms or lipophilic ethylenic groups to the surrounding medium (cf. Fig. 1b and c). The versatile solubility and transport capabilities of the crown ethers make them highly suited to applications as ionophores (phase transport catalysis) [10] or in sensing and signalling applications [11], often as a binding site in larger semiochemical devices [12–14]. On the other hand, much more rigidly preorganised ligands such as the spherands are suited to ion sequestration applications [8].

Of the alkali metal cations, K^+ is bound the most strongly in solution by almost all of the ethylenedioxy-based crown ethers [15] as a result of favourable chelate bite angle within the five-membered chelate ring. In the gas phase, however, it is Na^+ that is selected on charge density grounds [16]. In the solid state, however, binding equilibria and hence inter-ion selectivity are of only indirect relevance and structural features such as size and shape complementarity assume a greater importance. Furthermore, in solids, molecular geometry and indeed stoichiometry in labile crown ether based systems, is additionally subject to the operation of both directional and non-directional crystal packing forces. Because individual metal–crown ether oxygen interactions are often comparable in energy to crystal packing forces such as hydrogen bonds [17], a variety of interesting crystalline geometries are observed. This dependence on solid state effects allows crown ethers and their complexes with hard metal ions (in which the bonding is of the ion dipole type) to be considered under the umbrella of crystal engineering [18–20]. In other words it is possible to adopt a concerted approach to the rationalisation, and ultimately prediction of crown ether solid state structures, considering molecular and intermolecular interactions simultaneously. This allows the identification of conserved features (synthons [21]) from one structure to the next, and highlights the influence crystal packing forces may have on complex geometry. Such influences are much less apparent in more covalent systems in which the strength and directionality of the covalent bond is not significantly perturbed by solid state intermolecular interactions.

In this review a non-traditional view of traditional crown ether coordination chemistry of the alkali metals is examined. In particular the trade-off between first and second sphere coordination of hard metal cations by the crown ethers is examined with particular emphasis on hydrogen bonding interactions.

2. Crown ethers as first sphere ligands: size fit criteria

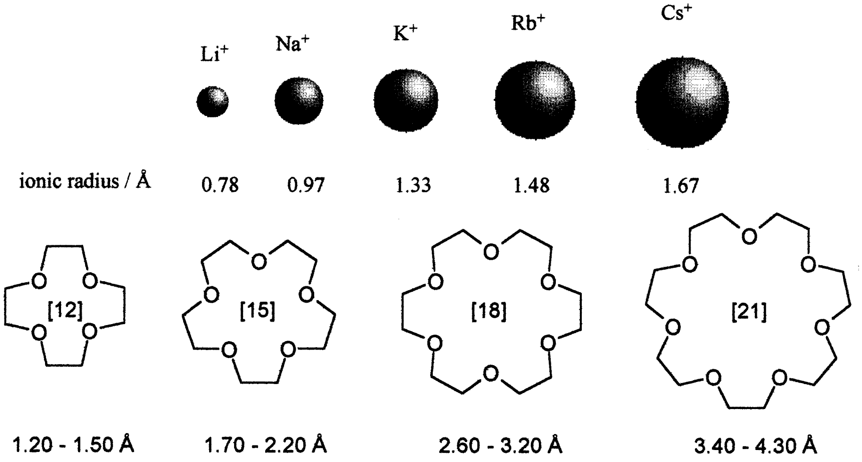
2.1. Sodium and potassium complexes of 18-crown-6

The ionic radii of the alkali metal cations along with approximate diameter of complementary crown ethers in idealised binding conformations is shown in Scheme 1. In the binding of such cations by various crown ethers Lehn [22] has distinguished two extreme possible situations:

1. 'Key' and 'lock' type complimentarity
2. Induced conformational adjustment

In the case of the flexible crown ethers the former case is rarely encountered since the adoption of symmetrical conformations such as the D_{3d} symmetry of 18-crown-6 (Fig. 1b) results in the generation of an unfavourable empty cavity. In the absence of guest ions other interactions, either with solvent or intramolecular hydrogen bonds take place, reducing the empty cavity volume (Fig. 1c).

The archetypal picture of a crown ether complex is the K^+ complex of 18-crown-6, shown free of additional solvent interactions in Fig. 1. In methanol (25°C) K^+ is bound by this ligand with a high stability constant, log K of 6.10, however in aqueous solution this drops to under 2 log units [23]. Clearly the solvation of the potassium cation is playing a significant part in the complexation equilibrium in solution. This is in part related to the fact that the crown ether is only a two



Scheme 1. Comparison of the ionic radii of alkali metal cations with crown ether cavity diameter.

dimensional ligand and leaves the ‘North and South poles’ of the metal cation exposed to other interactions, while it wraps about the ‘equator and tropics’. Nevertheless in the solid state $[K(18\text{-crown-}6)]^+$ is fully capable of adopting the centrosymetric structure shown in Fig. 1 in which the metal cation fits perfectly into the crown ether ligand. In the case of $[K(18\text{-crown-}6)][Cr(CO)_5Cl]$ **1** the K–O distances are around 2.78 Å [24]. Such desolvated complex cations are a common feature of ionic solids in which a lipophilic, non-coordinating cation is required. Other examples include [K(18-crown-6)] perchlorotriphenylmethanide [25], $[K(18\text{-crown-}6)](HCl_2)$ [26] and $[K(18\text{-crown-}6)]I_3$ [27], with K–O distances in the range 2.74–2.85 Å. The cation structure is strongly reminiscent of the direct size complementarity between metal and ligand surmised by Pedersen at the time of the first crown ether synthesis [2]. However, this symmetrical coordination mode is far from being the only coordination mode for this metal ligand combination. The structure of anhydrous $[K(18\text{-crown-}6)]NO_3$ (**2**) shows a conformation in which the metal cation ‘domes’ above the plane of the crown ether ligand in a similar fashion to porphyrin doming [28], proffering a greater exposed surface to the nitrate anion, which is coordinated in a bidentate fashion, Fig. 2 [29]. This is referred to as a ‘sunrise conformation’ [30]. The somewhat longer K–O distances are apparently a reflection of the fact that the metal ion is being pulled away from the most favourable intra-cavity site. The structure of the 2,6-dimethyl-18-crown-6 analogue is similar [31].

Such symmetrical or ‘domed’ structures are far from the only coordination modes available even to such a complementary combination as K^+ and 18-crown-6. A range of 2:2 species are known such as $[K_2(\mu_2\text{-}18\text{-Crown-}6)_2(\text{pyridyl})_2]$ bis((μ_2-

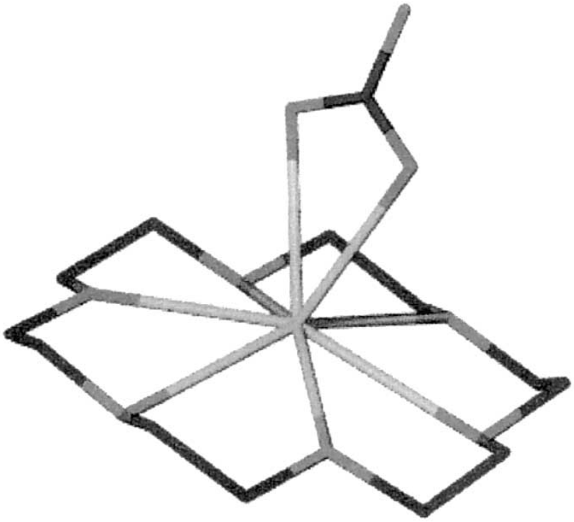


Fig. 2. X-ray crystal structure of $[K(18\text{-crown-}6)]NO_3$ (**2**) showing the doming of the cation above the crown ether plane. K–O distances 2.814–2.933 Å.

phenolato)-tetracarbonyl-titanium) (**3**) (Fig. 3) in which the crown ether ligand binds to one metal cation via six oxygen atoms and exhibits unidentate coordination to a second. Bond distances to the bridging oxygen atom are significantly longer [32]. Two analogous structures are known for benzo-18-crown-6 as a polyiodide [33] and $Hg_2I_6^{2-}$ salts [34] indicating that this solid state packing mode is tolerant of functional groups and counter anions. Bridging crown ether oxygen atoms are also found in the coordination polymeric [K_2(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)]$(OPh)_2$ (**4**) in which the potassium cations adopt a bis(perching) coordination mode, each binding to only four of the six crown ether oxygen atoms. Interestingly, the analogous Na^+ complex is also known and adopts a radically different structure, with the crown ether adopting a U-shaped conformation to wrap up half of the smaller Na^+ cations while a second Na^+ environment is coordinated solely by phenoxide ions, Fig. 4 [35]. A similar [Na_2(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)] dication to that encountered as the repeat unit in **4** is observed in the presence of Co(I) salen anions which also coordinate to the Na^+ cations via the salen oxygen atoms, Fig. 5 [36]. A more straightforward 18-crown-6

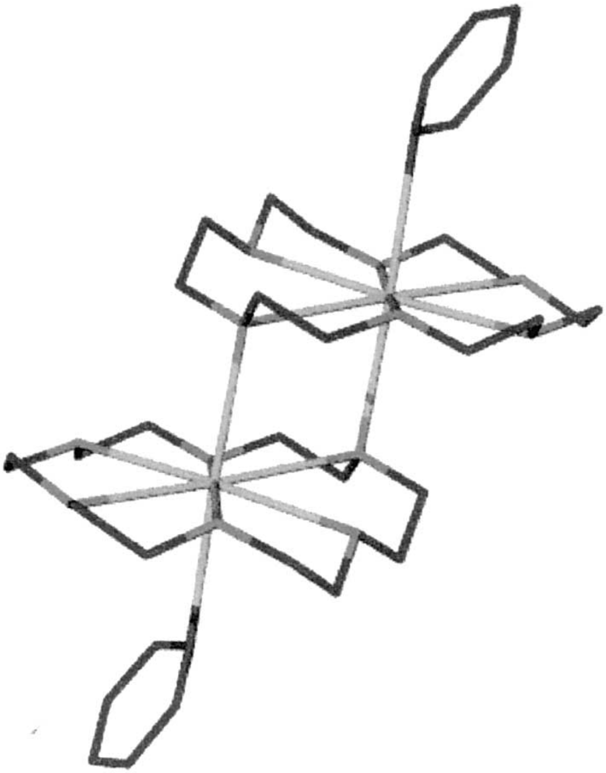


Fig. 3. K^+ 18-crown-6 2:2 complex in bis((μ_2-18-Crown-6)-pyridyl-potassium) bis((μ_2-phenolato)-tetracarbonyl-titanium) **3** [32].

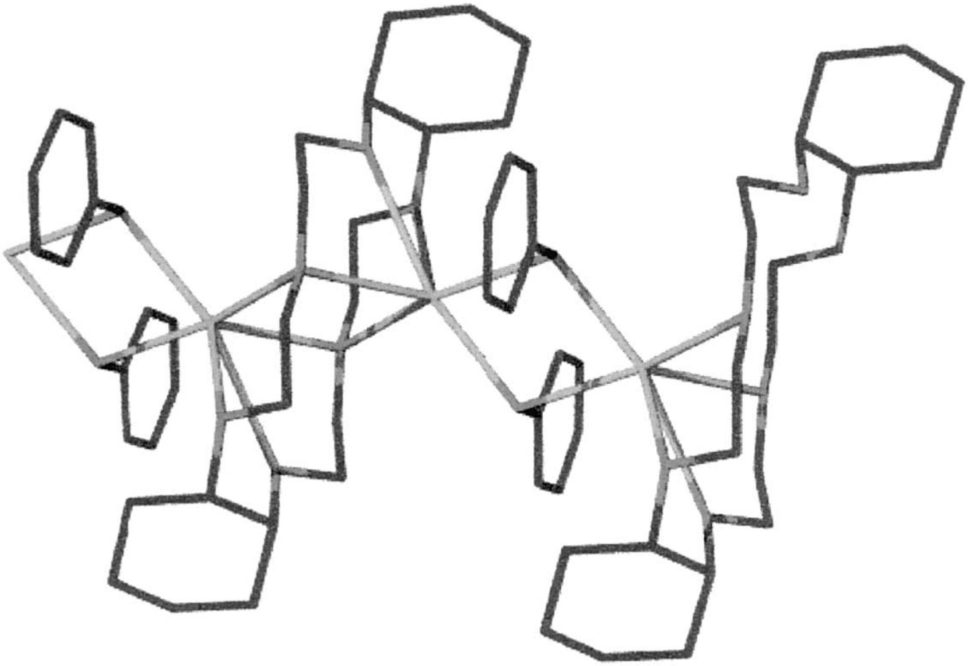


Fig. 4. The coordination polymeric [K_2(*cis*-*anti*-*cis*-dicyclohexyl-18-crown-6)]$(OPh)_2$ (**4**) [35].

bridged species [K_2(18-crown-6)$_3$][W_2(μ-H)(μ-O)(O*t*-Bu)$_6$] (**5**) resembles the nitrate complex **1** with the K^+-coordinated nitrate ligand replaced by a bis(bidentate) 18-crown-6, Fig. 6 [37]. An analogous η^6:η^2 bis(18-crown-6) potassium cation has also been reported [38]. Remarkably, the much smaller 15-crown-5 can also bridge between two potassium ions in [K_2(15-crown-5)](pyridine-2-thiolate)$_2$ (**6**), Fig. 7 [39].

More common than bridging coordination modes of 18-crown-6 is the expansion of the K^+ coordination sphere by the addition of solvent molecules thus, in addition to the six-coordinate structure observed in Fig. 1b, seven-, eight- and nine-coordinate potassium ions are known. The structure of [K(H_2O)(18-crown-6)]$^+$ 4,4-bis(trifluoromethyl)-2,2,2-triphenyl-3-phenylthio-1-oxa-2-stannetanide (**7**) is ostensibly seven coordinate but also contains a long K–F contact of 3.06 Å. This may be the result of a specific K–F interaction, or it may arise from the hydrogen bonding of the coordinated water molecule to the oxygen atom of the tin-containing anion, Fig. 8 [40]. Potassium–fluorine coordination interactions are also observed in the KPF_6 salt of *N*-allylaza-15-crown-5, with K–F distances in the range 2.90–2.98 Å [41]. In this case the ligation by fluorine is assisted by ion–ion interactions. Work on alkali metal complexes of fluorinated spherands suggests that there is no specific attractive interaction between the contracted lone pairs of a fluoro substituent and alkali metal cations [42]. However, Na–F contacts as short as 2.374 Å have been observed when supported by other metal–dipole interactions,

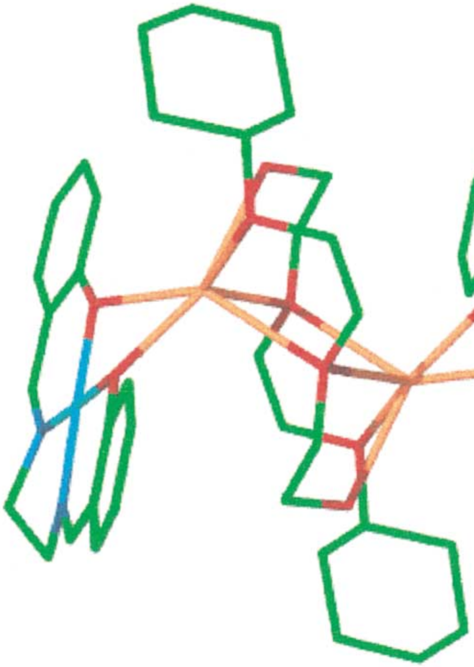


Fig. 5. $[Na_2($*cis-anti-cis*-dicyclohexyl-18-crown-6)] as the *N*,*N*′-ethylene-bis(salicylideneaminato)-cobalt salt [36].

as in the sodium perchlorate complex of the fluoro substituted aryl crown ether **9**, Fig. 9 [43].

The exposed north and south poles of 18-crown-6 encapsulated metal cations allows the possibility of solvent coordination both above and below the plane of the macrocycle complex and both K^+ and Na^+ form bis(solvates) with oxygen donors such as thf in which the O_{thf}–M–O_{thf} vector is essentially linear and normal to the plane of the MO_6 equator, e.g. $[Na(thf)_2(18\text{-crown-}6)][W(CO_5)Me]$ (**10**) [44] and $[K(thf)_2(18\text{-crown-}6)]X$ (**11**) ($X = [\{Cd(C_6F_5)(\mu_2\text{-}SCPh_3)\}_3(\mu_3\text{-}OH)]$ [45] and bis((2,2,7,7-tetramethyl-3,6-diazaoct-4-en-3,6-diyl)-gallium) [46]), Fig. 10. The M–O_{crown} distances in the sodium complex of 2.73–2.79 Å are almost identical to those found in the K^+ analogue (2.73–2.82 Å). In contrast the thf molecules are significantly closer to the Na^+ cation than K^+ (2.33 vs. 2.73–2.91 Å av.), clearly suggesting that the Na–O_{crown} distances are imposed by the minimum crown diameter attainable without the introduction of significant O···O repulsions, rather than the coordination requirements of the Na^+ cation. Interestingly, the analogous bis(solvate) complex of *iso*-propyl alcohol, $[K(iPrOH)_2(18\text{-crown-}6)]^+$ (**12**) in the presence of bis(*N*,*N*′-ethylenebis(acetylacetonylideneiminato))-tetrakis(μ_2-cyano)-di-cyano-iron-di-manganese(III) anion adopts a similar eight coordinate geometry, however the $O_{alcohol}$–K–$O_{alcohol}$ vector is no longer normal to the crown ether equatorial plane and forms an angle of 73° to it, apparently as a result of intermolecular hydrogen bonding to the anion [47]. An unusual nine-coordinate potassium 18-crown-6 trihydrate has also been reported, $(H_3O)[K(H_2O)_3(18\text{-crown-}6)]Cl_2 \cdot H_2O$ (**13**). In this case the crown ether adopts a markedly U-shaped conformation in order to expose sufficient surface of the K^+ ion to accommodate three additional ligands. Potassium–crown distances are all remarkably short, however, as the crown ether wraps around the metal cation, Fig. 11 [48].

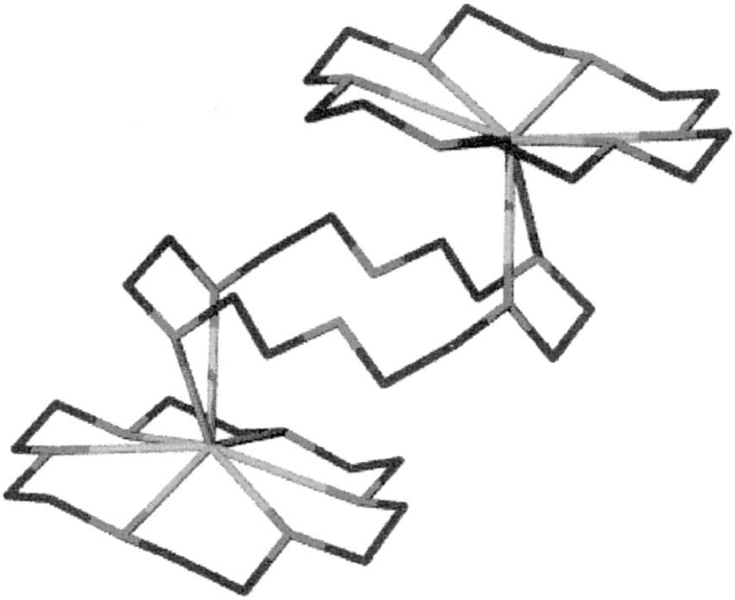


Fig. 6. The $[K_2(18\text{-crown-}6)_3]^{2+}$ cation in **5** [37].

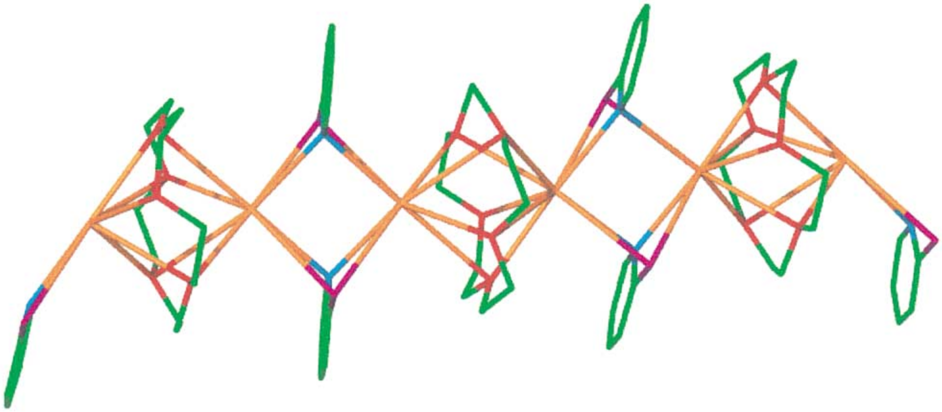


Fig. 7. The small 15-crown-5 bridging between two large K^+ ions in **6** [39].

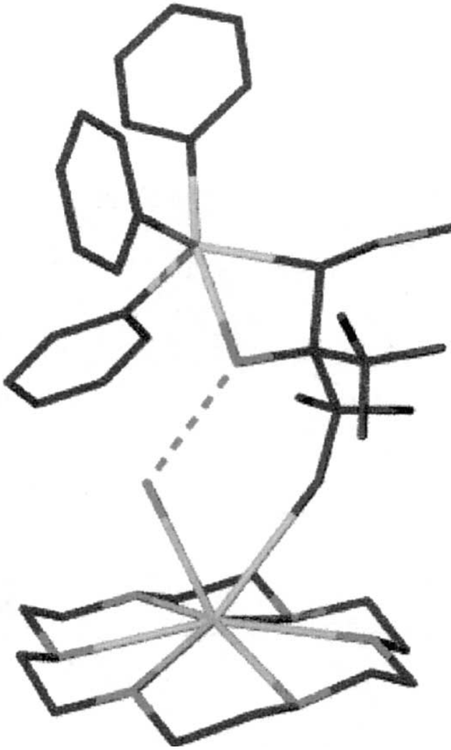
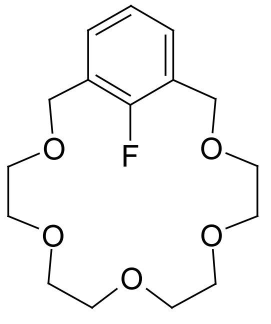


Fig. 8. A long K–F interaction in the seven coordinate complex **7** [40].

The conformation of the 18-crown-6 ligand in **13** indicates that very significant deviations away from the centrosymmetric conformation shown in Fig. 1b are possible. This is consistent with the flexibility of the macrocycle and arise as a consequence of the complex ion geometry (and identity of additional ligands) and the solid state environment in which the complex finds itself. A similar U-shape deformation is observed in the $[K(18\text{-crown-}6)]^+$ salt of bis(naphthalene-1,8-diolato)-phenyl-silicate **14** in which the K^+ ion is markedly extruded from the crown ether in order to interact with the oxygen atoms of the napthalenediolate. In this case $K{-}O_{crown}$ distances are long, consistent with the bulky nature of the silicate anion, Fig. 12 [49]. A less marked cup-shaped conformation is also seen in the potassium dibenzo-18-crown-6 complex of $[Co(CO)_3(CO_2Me)_2]^-$. Consistent with the smaller distortion $K{-}O_{crown}$ distances are intermediate between those found in **13** and (**14**) [50]. Indeed such a 'sunrise' conformation appears to be favoured in any case in which there is a significant K^+–anion interaction, as in the lovely C_3 symmetric $[K(18\text{-crown-}6)]_3[Ir(Ge_4)_3]$ (**15**) [51].

Despite these distortions it is probably fair to say that K^+ and 18-crown-6 are an excellent match under most circumstances and thus the question arises as to what happens when there is less perfect complementarity between metal cation and



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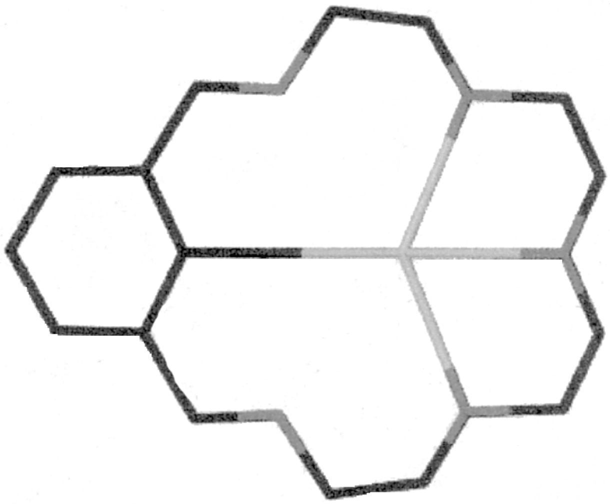


Fig. 9. Sodium complex of fluoro-crown **9** [43].

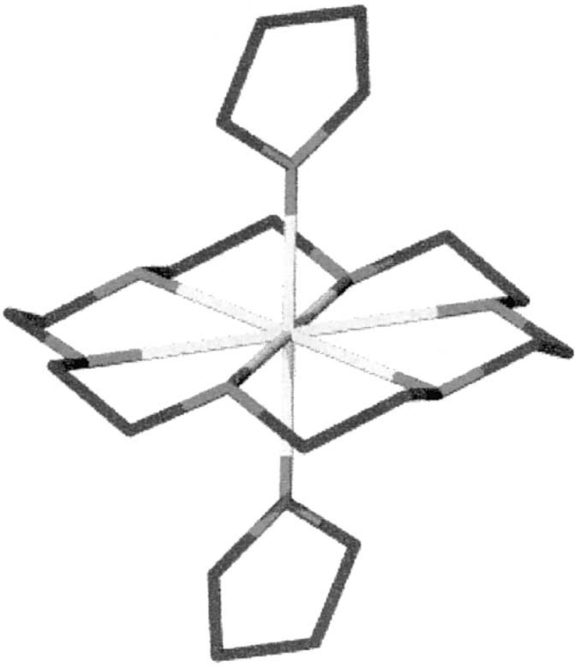


Fig. 10. $[Na(thf)_2(18\text{-crown-}6)]^+$ [44,46].

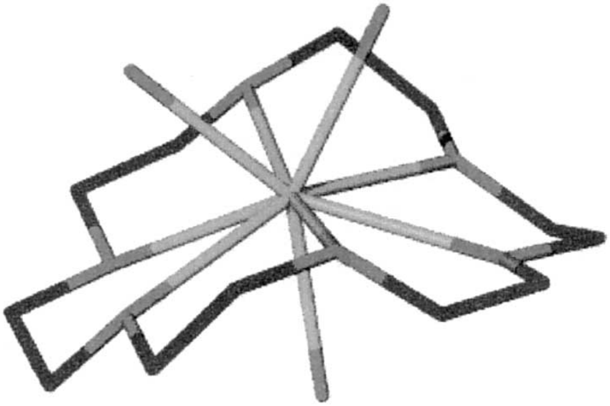


Fig. 11. The nine-coordinate $[K(H_2O)_3(18\text{-crown-}6)]^+$ cation in **13** [48].

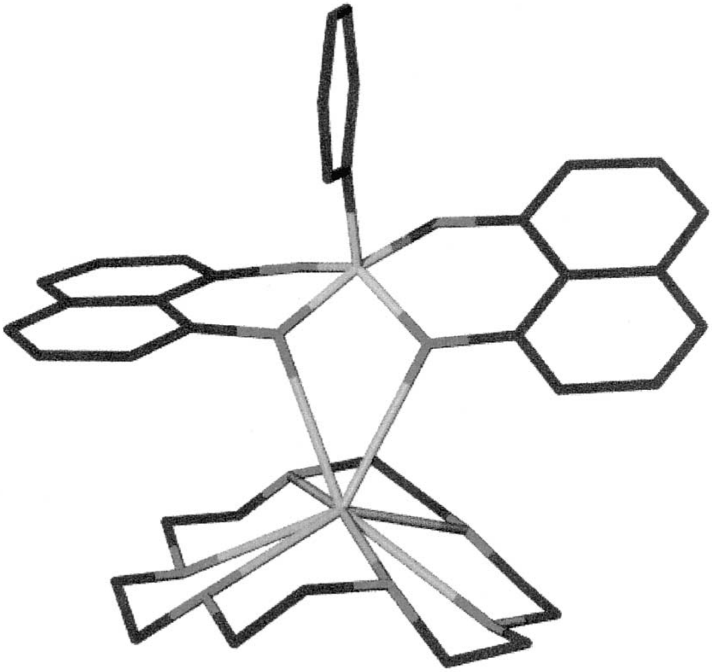


Fig. 12. Extrusion of K^+ away from the crown ether plane in **14** [49].

ligand? In the case of many transition metal complexes of the crown ethers second sphere coordination via hydrogen bonding to coordinated water is frequently observed as a consequence of the smaller size of first row transition metal M^{2+} ions [52]. However, in the case of Na^+ there is still a reasonable match, as seen for the thf complex **10**, although marked differences in behaviour can arise from the smaller ionic radius of Na^+, e.g. compound **4** and its Na^+ analogue. In fact there are four possible responses of a metal cation when faced with a large non-complimentary macrocyclic ligand diameter [53]. These are:

1. The metal cation sits at the centre of the ligand with non-optimal M–O distances (2.8 Å in the case of Na^+ and 18-crown-6 and its derivatives). This is observed for (Rb^+,Na^+)dibenzo-18-crown-6 [54].
2. The metal cation deviates from the centre, making shorter contacts with some donor atoms and longer ones with others. This is observed for the $NaBr{\cdot}2H_2O$ complex of dibenzo-18-crown-6 [55].
3. The metal cation exhibits dynamic or static crystal disorder, exemplified either by large anisotropic displacement parameters or resolvable, discrete cation positions within a static ligand framework, e.g. $[Na(H_2O)_2(18\text{-crown-6})]N_3$ [56].
4. The crown ether distorts to adopt a conformation more complementary to the metal cation's coodination requirements, e.g. the NaBr complex of *cis*-*anti*-*cis*-dicyclohexyl-18-crown-6. in which the crown ether adopts an elliptical shape with short Na–O contacts in the centre an much longer distances at the ends [57].

An example of extreme conformational distortion is observed in the $[Na(18\text{-crown-}6)]^+$ complex of iron(III) tetraphenylporphyrin bis(pentafluorophenylthiolate) anion in which a thiolate occupies one face of the Na^+ while the crown ether distorts to cover the remaining side with one of the oxygen atoms, Fig. 13 [58]. An approximately similar conformation is observed in $[Na(H_2O)(18\text{-crown-6})](SCN)$ (Section 3) [59], while in the dicyclohexyl-18-crown-6 complex of sodium phenoxide phenol clathrate the crown ether almost doubles back on itself, exhibiting a mixture of short (2.45 Å) and intermediate Na–O distances, Fig. 14 [60]. The K^+ analogue exhibits a much more symmetrical conformation. In contrast, in the Na^+ 18-crown-6 complex with $[U(\eta^5\text{-}C_5Me_5)_2(t\text{-BuS})(S)]^-$ (**16**) the crown ether binds to Na^+ via only five oxygen atoms, with widely varying Na–O distances from an optimum 2.45 Å to longer distances at 2.7 – 2.8 Å. The uncoordinated oxygen atom is 3.28 Å from the metal ion, Fig. 15 [61]. In contrast to all these results, the Na^+ 18-crown-6 unit in the analogous complex with $P(CN)_2Br_2^-$ exhibits the D_{3d} centrosymmetric conformation [62].

2.2. Coordination to Rb^+ and Cs^+

In contrast to Na^+, Scheme 1 shows that Rb^+ and Cs^+ are somewhat too large to fit comfortably and centrosymmetrically within the cavity of 18-crown-6 and its derivatives and are therefore much more likely to adopt 'sunrise' conformations or even sandwich structures in which a single cation is held between a pair of crown ether ligands. In fact, in the case of Rb^+ complexes of 18-crown-6 work by Domasevitch et al. has revealed complexes in which (i) the large cation is held perfectly within the crown ether cavity, (ii) is disordered over two possible sunrise positions, each only 0.276 Å out of the plane of the D_{3d} crown ether or (iii) adopts a more typical sunrise conformation. In the former case the $[Rb(18\text{-crown-6})]^+$

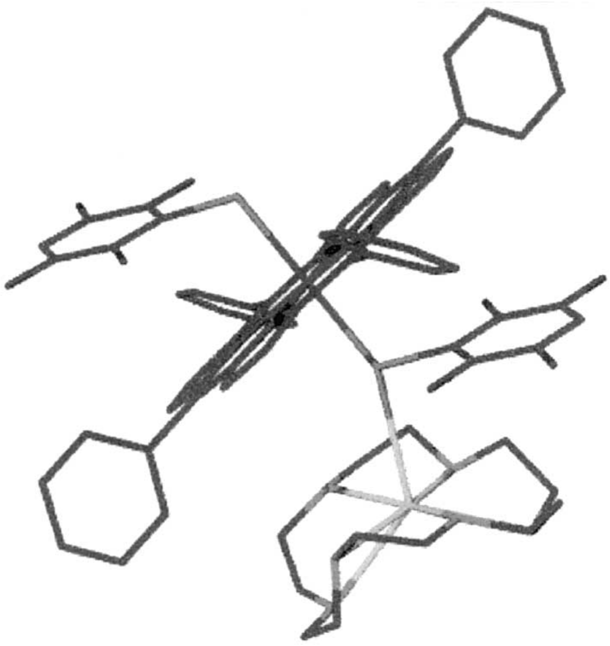


Fig. 13. Folded [Na(18-crown-6)]$^+$ as the counter ion to a bis(C_6F_5S) complex of iron(III) tetraphenyl porphyrin [58].

moiety is stabilised by centrosymmetric counter ions $\{H(ONC(CN)R)_2\}^-$ (R = COPh, benzothiazol-2-yl). A similar structure is observed for Tl^+ which has a similar ionic radius [30]. The disordered case is observed with $AuCl_4^-$ anions and apparently arises as a consequence of weak interactions with the chloride ligands to form an infinite chain [63]. The analogous $Au(CN)_4^-$ complex is ordered, however, with the Rb^+ ion situated 0.90 Å out of the plane of the crown ether ligand. Rb–O distances are in the range 2.93–3.17 Å [63].

Sunrise geometries are noted for both the Rb^+ and Cs^+ 18-crown-6 complexes with the $N(PPh_2)_2^-$ anion with the Cs^+ cation rising significantly further from the plane of the crown ether than in the Rb^+ case. Interestingly these two structures illustrate much softer nature of the Cs^+ cation and its tendency to engage in cation–π interactions. The Rb^+ ion interacts with the phosphorus atoms of the anion, while the Cs^+ ion is closest to one of the phenyl rings, Fig. 16 [64].

Not even Domasevitch's group have been able to make Cs^+ fit centrosymmetrically within 18-crown-6 and in the presence of relatively non-coordinating anions it commonly forms 2:1 sandwich complexes as in [Cs(18-crown-6)$_2$]X and [Cs(18-crown-6)(15-crown-5)]X ($X = e^-$, Na^-) [65] or even the 'club sandwich' [Cs$_2$(18-crown-6)$_3$]$^{2+}$ in the case of the complex with the α-cyanobenzothiazole-α-carbaldehyde oximate anion, Fig. 17 [66]. The Cs···Cs distance in this complex is 4.335 Å, however distances as short as 3.940 Å have been observed for bridging

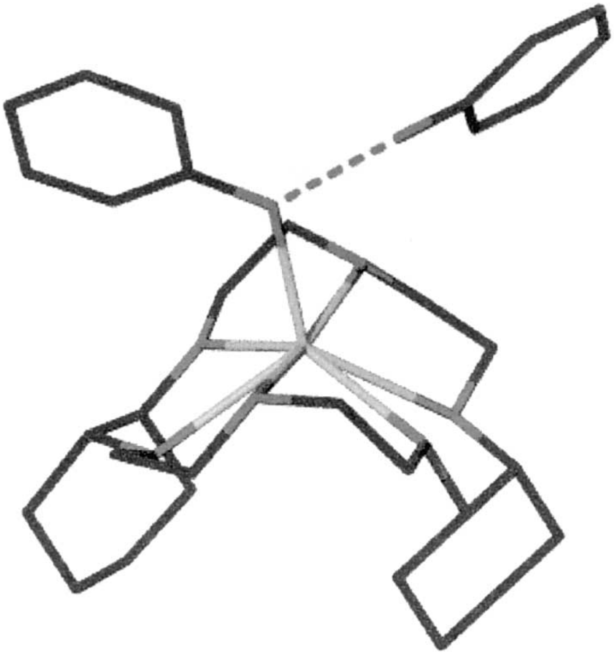


Fig. 14. Wrapping conformation of dicyclohexyl-18-crown-6 as the sodium phenoxide phenol clathrate [60].

18-crown-6 ligands, as in [Cs_2(18-crown-6)][(p-MeC_6H_4)N=NNN=N(C_6H_4Me-p)]$_2$ [67]. In the absence of crown bridges, distances between Cs^+ ions are longer; 5.117 Å in the case of [Cs(18-crown-6)(SCN)]$_2$, Fig. 18. Interestingly the SCN^- ligands in this complex coordinate to the soft Cs^+ ions via the hard nitrogen end of the ambidentate ligand [68]. This effect may be attributable to space-filling crystal packing constraints, since no short S···S contacts are observed. A related aqua-bridged complex has been reported recently with a Cs···Cs contact of 5.334 Å in which the bridging water molecules hydrogen bond to dicyanamide anions to give a hydrogen bonded network structure [69].

2.3. Complexes of Li^+

The very small size of Li^+ means that it is too small to fit within all but the smallest crown ethers. Even with 12-crown-4 2:1 sandwich complexes such as [Li(12-crown-4)$_2$]($AsPh_2$)·thf (**17**), Fig. 19, are commonly observed [70]. Similar complexes are known with Na^+ albeit with somewhat longer M–O distances. In these cases the small macrocycle does not impose any constraints on the attainable M–O distances [71]. 12-Crown-4 can also act as an unsymmetrical bridging ligand for Li^+, forming a 2:2 sandwich complex in the presence of the [$MoNCl_4$]$^-$ anion **18**, Fig. 20. The Li···Li non bonded contact is 3.107 Å and interestingly the bridging

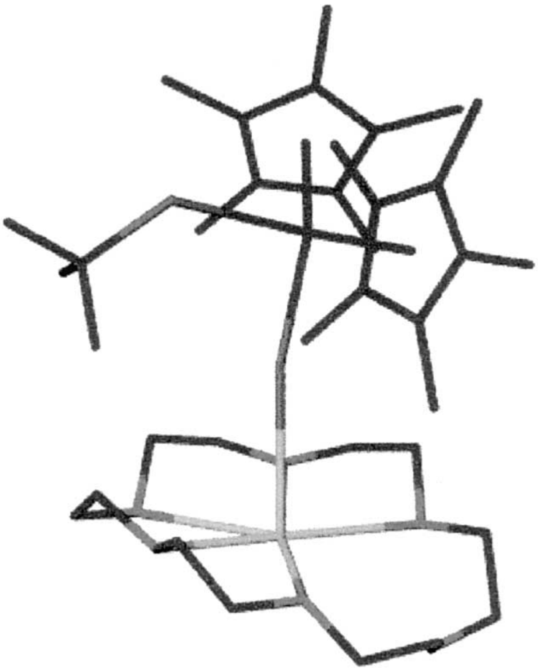


Fig. 15. 18-Crown-6 bound via five oxygen atoms in **16** [61].

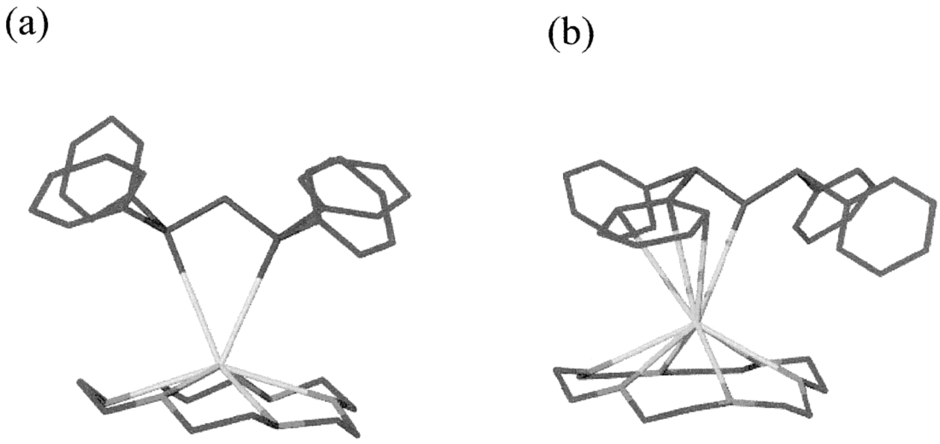


Fig. 16. (a) $[Rb(18\text{-crown-}6)]^+$ and (b) $[Cs(18\text{-crown-}6)]^+$ complexes of $N(PPh_2)^-$ [64].

oxygen atom forms a much closer contact to the Li^+ to which the macrocycle binds through only one oxygen atom (2.008 Å) than the distance to the bridging oxygen within the tetrahapto unit (2.341 Å), reminiscent of an η^3:η^1 coordination mode for

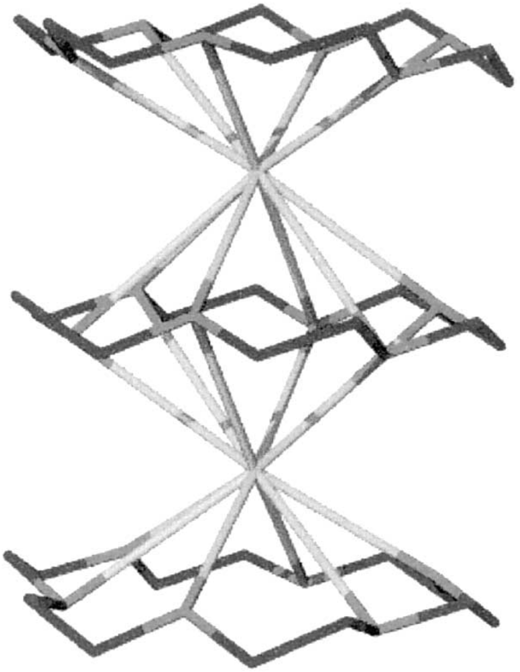


Fig. 17. The $[Cs_2(18\text{-crown-}6)_3]^{2+}$ club sandwich [66].

each 12-crown-4 ligand [72]. With 15-crown-5, Li^+ fits well into the macrocyclic cavity with only a slight doming observed for $[Li(15\text{-crown-}5)][InCl_4]$ (**19**), Fig. 21. Lithium–oxygen distances are in the range 2.08–2.28 Å [73].

18-Crown-6 complexes of Li^+ commonly incorporate more than one metal cation or coordinated solvent that fills the remainder of the cavity (see Section 3.1). This point is well illustrated by the 1:2 18-crown-6 complex of lithium phenoxide in which two Li^+ ions are encapsulated in a fashion coplanar with the six oxygen atoms within a D_{3d} symmetric crown, Fig. 22 [74]. The Li···Li distance is only 2.35 Å. A compound of similar 1:2 stoichiometry is also observed for the $Li(BH_4)$ adduct of 18-crown-6 although in this case the crown ether is dramatically distorted from the D_{3d} conformation, resulting in a much longer Li···Li distance of 3.368 Å [75]. The Li^+ ions engage in unconventional B–H···Li hydrogen bonds of the type termed intermolecular pseudo-agostic (IPA) by Braga et al., Fig. 23 [18]. IPA interactions to alkali metal cations are also observed for transition metal hydrides with $[RuH_3(PPh_3)_3]^-$ interacting with a slightly domed potassium 18-crown-6 complex via two of its three hydrido anions [76]. The osmium analogue is more symmetrical with all three Os–H moieties within bonding distance of the potassium [77].

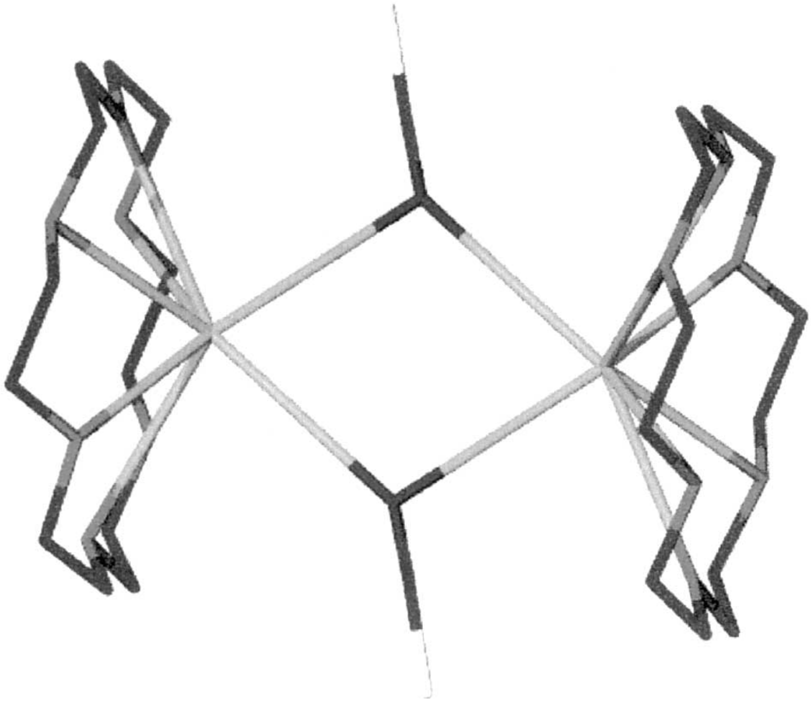


Fig. 18. [Cs(18-crown-6)(SCN)]$_2$ [68].

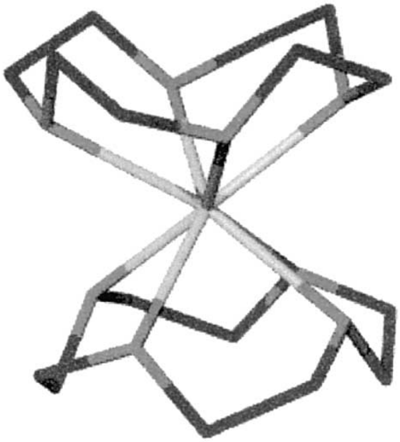


Fig. 19. Sandwich complex of Li$^+$ and 12-crown-4 in **17** [70].

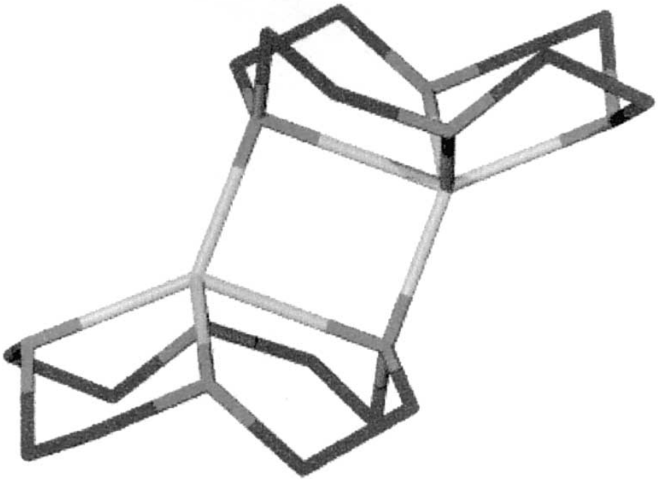


Fig. 20. Sandwich containing two Li^+ ions and two 12-crown-4 molecules in **18**. Note the doming of the Li^+ ions out of the plane of the macrocycle [72].

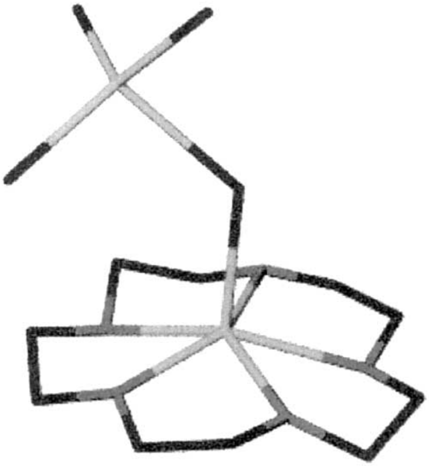


Fig. 21. Good fit between Li^+ and 15-crown-5 in **19** [73].

2.4. Larger crown ethers

In much the same way as more then one lithium ion can fit within 18-crown-6, larger crown ethers are able to encapsulate more than one of the larger alkali metal cations, except in circumstances in which they are able to ‘wrap up’ a single cation, often entirely isolating it from the surrounding medium. In the case of dibenzo-30-crown-10 such a ‘wrapping’ complex is formed with KSCN [78] with the crown

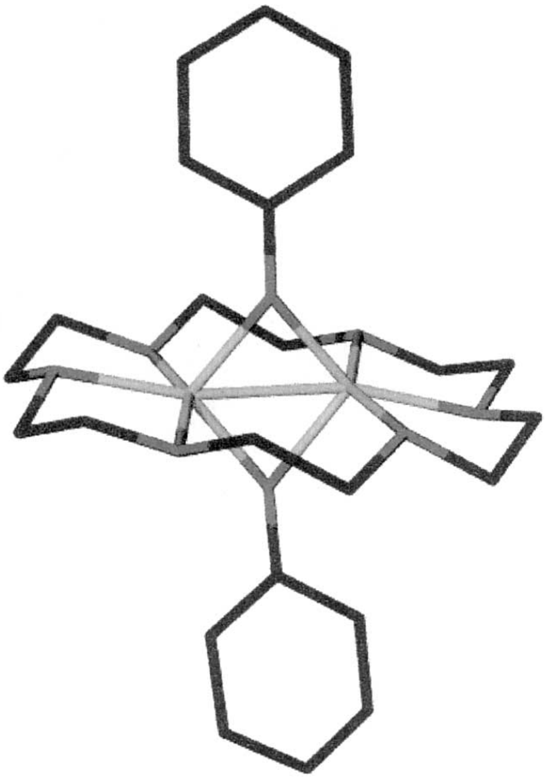


Fig. 22. Inclusion of two Li^+ ions within 18-crown-6 (phenoxide salt).

ether entirely changing conformation from the free state upon complexation, Fig. 24. The analogous NaSCN complex, however, is a 1:2 complex with the crown ether behaving effectively as an open bis(15-crown-5), Fig. 25 [79]. Interestingly, despite the smaller size of dibenzo-24-crown-8 this also forms a 1:2 complex, this time with KSCN, Fig. 26 [80]. A similar structure is observed for the potassium salicylate complex, which actually co-crystallised with a 1:2 sodium analogue, Fig. 27 [81]. Clearly, in the case of larger crown ethers the flexibility of the crown ether as much as size and preorganisation is of paramount importance. The same ligand is able to wrap around a single Cs^+ ion in the 1:1 complex with $Cs[Ag(CN)_2]$, although clearly even Cs^+ is too small to fit within this large crown ether in a planar fashion, Fig. 28 [82]. Derivatives of 24-crown-8 are also able to wrap up Na^+ in much the same way as dibenzo-30-crown-10 wraps up K^+, as observed for the sodium perchlorate complex of *cis*-*syn*-*cis*-dicyclohexano-24-crown-8, Fig. 29 [83]. Conversely, a small change in the size of the crown ether to a 26-membered ring gives a striking 1:4 coordination polymeric complex with NaI, Fig. 30 [84]. The vast dibenzo-36-crown-12 forms a 1:2 complex with $NaPF_6$ with the crown ether organising itself into two 15-crown-5 like domains, Fig. 31 [85]. The analogous

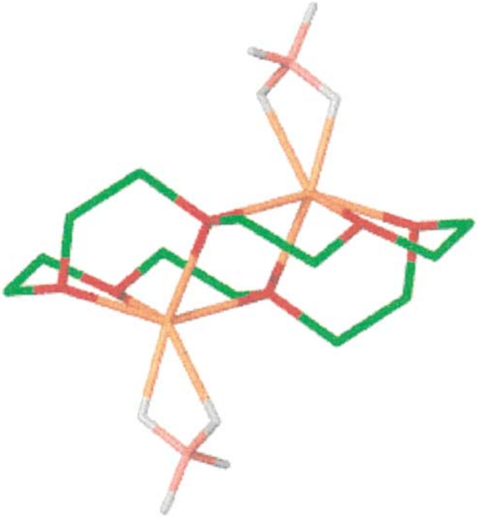


Fig. 23. $Li(BH_4)$ complex of 18-crown-6 [75].

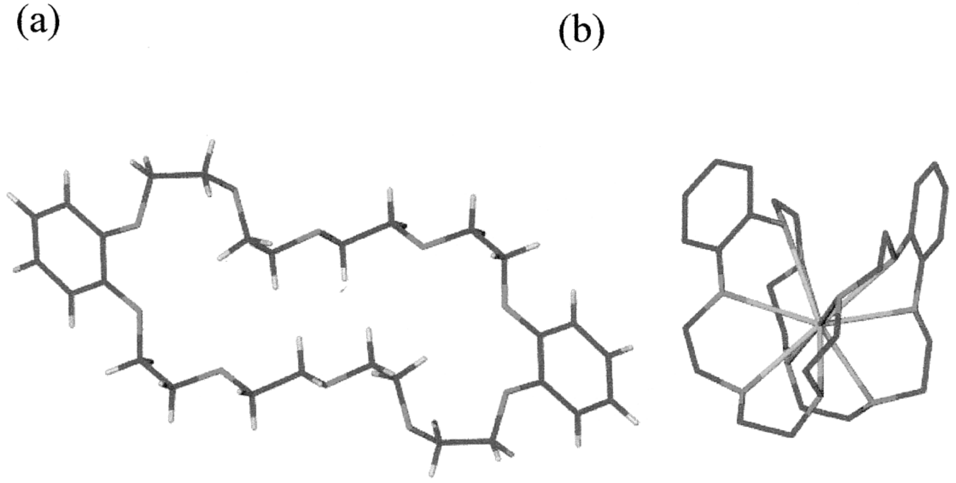


Fig. 24. (a) Crystal structure of free dibenzo-30-crown-10, (b) encapsulation of K^+ by dibenzo-30-crown-10 [78].

lithium picrate complex involves the organisation of the ligand into two 18-crown-6 like domains in order to maximise intramolecular hydrogen bonding, See Section 3.1 [86].

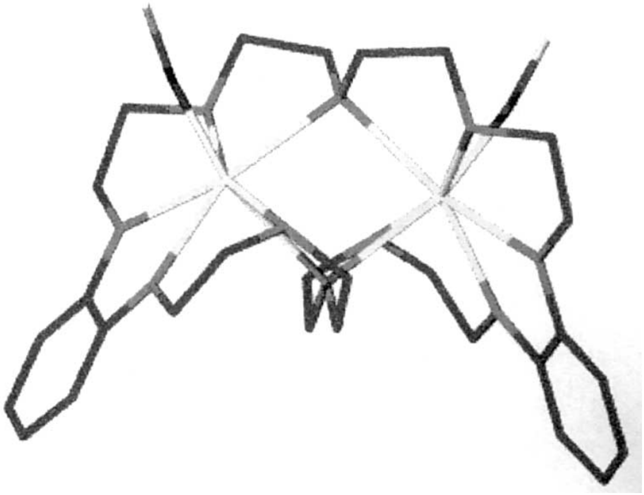


Fig. 25. Disodium complex of dibenzo-30-crown-10 in which the ligand behaves as a double 15-crown-5 [79].

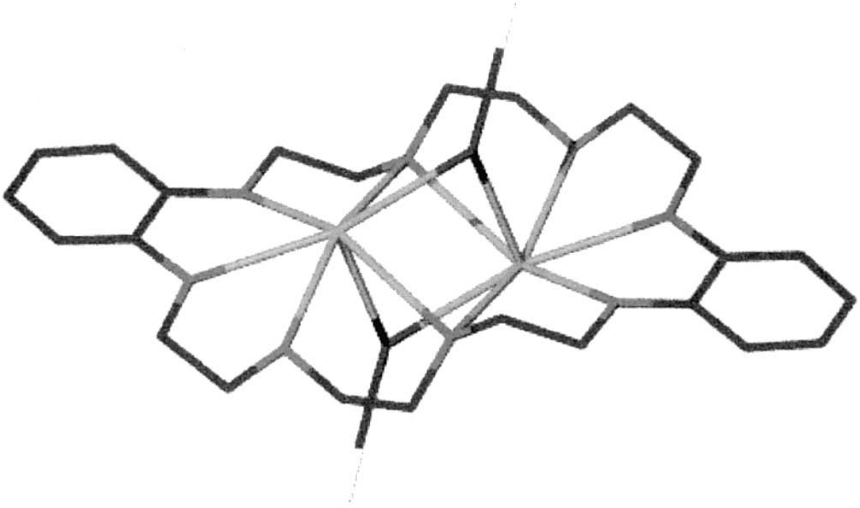


Fig. 26. Dibenzo-24-crown-8 1:2 complex with KSCN. Note the contrast to Fig. 24 [80].

2.5. Chelate ring size effects

So far we have looked at almost exclusively ethylenedioxy-based crown ethers, which result in the formation of five-membered chelate rings that are least strained for metals about the size of K^+, Fig. 32 [9]. Six-membered chelate rings are more suitable for smaller metal ions such as Li^+, thus 14-crown-4 forms much more

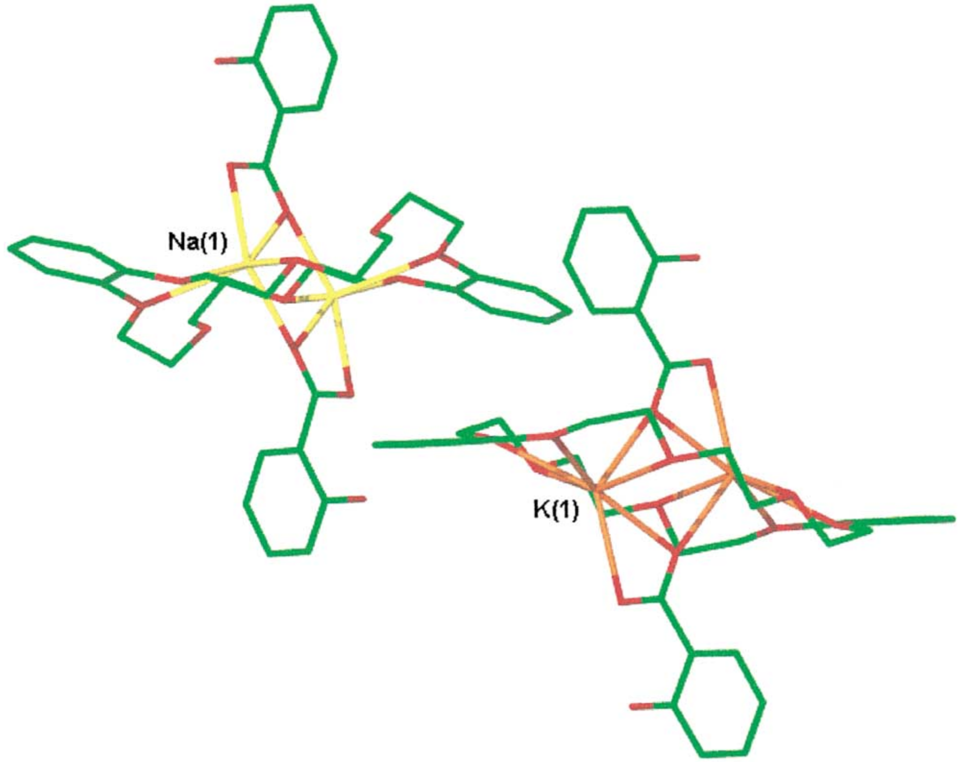


Fig. 27. Co-crystal of the 1:2 sodium and potassium salicylate complexes of dibenzo-24-crown-8. Note the more 'wrapped' structure in the sodium complex [81].

stable complexes with Li^+ and Na^+ than 12-crown-4 [6,15]. The effects of chelate ring size are evident in the 20-crown-6 derivative of KSCN in which the two oxygen atoms forming a seven-membered chelate ring adopt a markedly twisted conformation in order to minimise bite angle. Despite this the bite angle is 66° compared to 57–60° for the five-membered chelate rings in the complex, Fig. 33 [87]. In the sodium isothiocyanato complex of 15,15-bis(dodecyloxymethyl)-16-crown-5 the six membered chelate ring, more suitable for Na^+, exhibits a large bite angle of 77.16° while the less favourable five-membered rings open up to 66–70°, Fig. 34 [88]. The eight-membered chelate ring in the analogous 18-O_5-(2,2′)-diphenylmethano-2_4-coronand-5 complex shows evidence of severe strain both in the orientation of the diphenylmethane moiety and in the large bite angle of 82.63°, Fig. 35 [89]. The lithium complex of dicyclohexyl-13-crown-4, [Li(NCS)(dicyclohexyl-13-crown-4)] (**20**), shows a very large chelate bite angle of 91.95° for the six-membered ring, with angles of 78–79° even for the five-membered rings, Fig. 36 [90]. Such large bite angles are typical for lithium complexes with the analogous perchlorate complex of **20** showing similar parameters while the larger 18,18′-spiro-bis(19-crown-6) bis(lithium) bis(iodide) tetrahydrate (**21**) shows the Li^+ ions bound to one side of the large

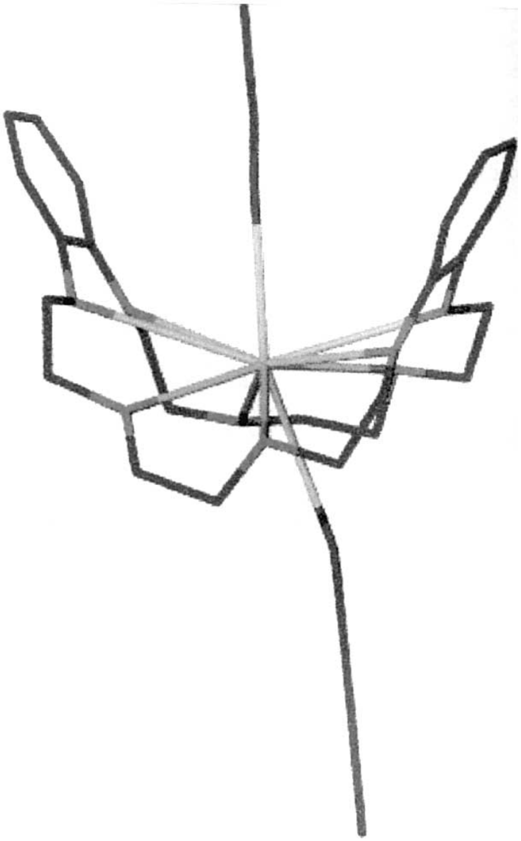


Fig. 28. Caesium complex of dibenzo-24-crown-8 [82].

fused macrocyclic rings forming a five and six-membered chelate with bite angles of 79.95 and 91.28°, Fig. 37 [91].

3. Simultaneous first- and second-sphere coordination

A number of transition metal, lanthanide and actinide aquo species readily form hydrogen bonded complexes with crown ethers acting as second sphere ligands [92]. Indeed, the ability of water molecules or hydrated oxonium ions to take the place of metal cations in crown ether chemistry is well documented. Numerous studies have shown that 18-crown-6 is selective for H_3O^+ which is included neatly into the macrocyclic cavity in the D_{3d} conformation forming three bifurcated hydrogen bonding interactions [24,26,93]. The larger 21-crown-7 binds $H_5O_2^+$ while dibenzo-30-crown-10 selects two H_3O^+ ions [94]. Smaller crown ethers form hydrogen bonded polymers or oligomers with 15-crown-5, forming an alternating infinite chain of crown ether acceptors and $H_7O_3^+$ ions in the presence of $AuCl_4^-$ [95]. In

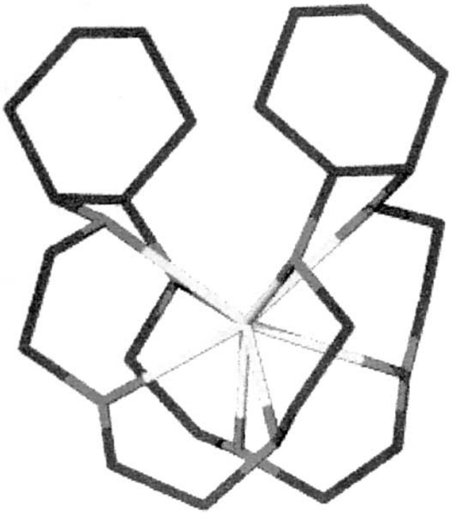


Fig. 29. Sodium perchlorate complex of *cis-syn-cis*-dicyclohexano-24-crown-8 [83].

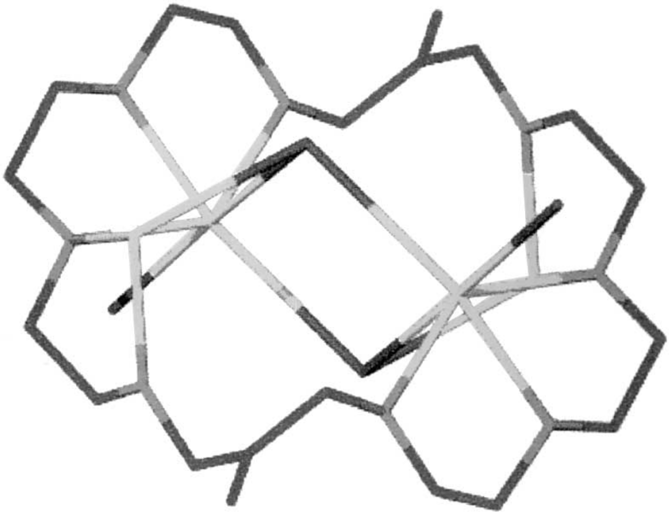


Fig. 30. Binding of four Na^+ ions by a 26-crown-8 derivative [84].

non acidic media crown ethers form numerous hydrates, a testament to their ability to act as hydrogen bond acceptors [96]. It is not surprising, therefore that in cases where small metal ions are crystallised from aqueous or 'wet' solutions in the presence of larger crown ethers incorporation of water may occur. Interestingly, because the strength of a moderate O–H···O hydrogen bond [17] is comparable to the type of ion-dipole interactions involved in alkali metal ion complexation,

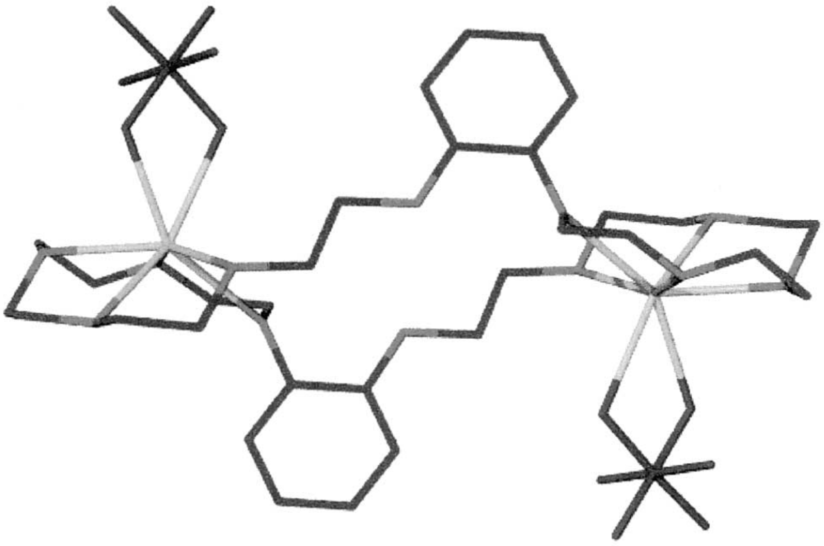


Fig. 31. Two five-coordinate domains are sufficient to bind two Na^+ ions in the 1:2 complex of $NaPF_6$ with dibenzo-36-crown-12 [85].

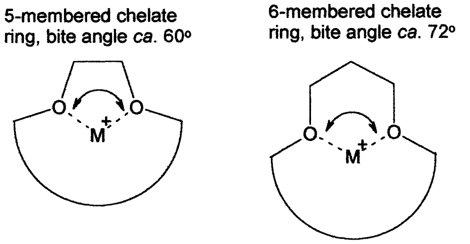


Fig. 32. Relationship between chelate ring size and chelate bite angle. Ligands with a small bite angle are stabilised by larger metal ions such as K^+.

hydrogen bonding to incorporated water molecules and indeed intermolecular interactions in general, may have a very significant effect on the structures of mismatched alkali metal crown ether complexes. In crystal engineering terms crown ethers are moderately strong hydrogen bond acceptors but have very little donor capability (although the acidic CH_2 groups form numerous weaker C–H···X interactions) [97]. Thus, while the coordination requirements of the metal cation discussed in Section 2 remain, we have seen that they may be satisfied in a wide variety of different ways. The simultaneous satisfaction of the crown ether and included solvent hydrogen bonding requirements may well determine the overall complex geometry and/or stoichiometry.

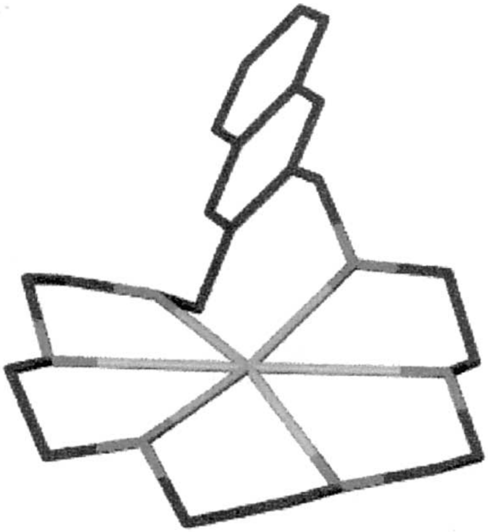


Fig. 33. Minimisation of the bite angle of the seven membered chelate ring in the KSCN complex of napthyl 20-crown-6 [87].

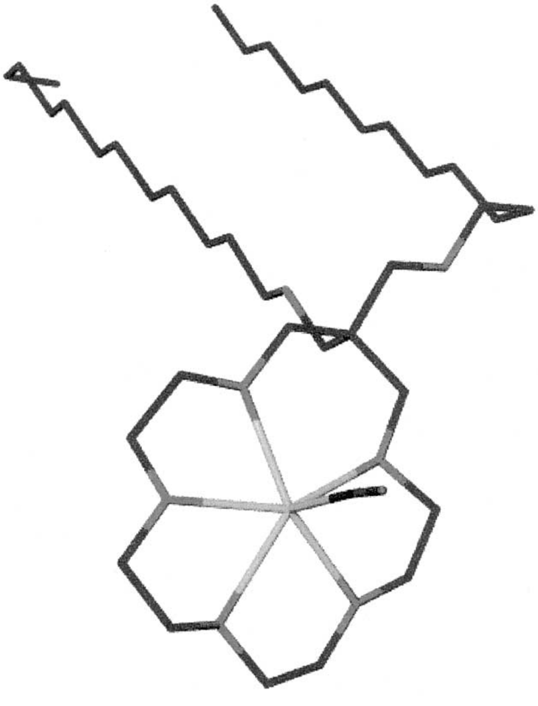


Fig. 34. Sodium-containing six- and five-membered chelate rings [88].

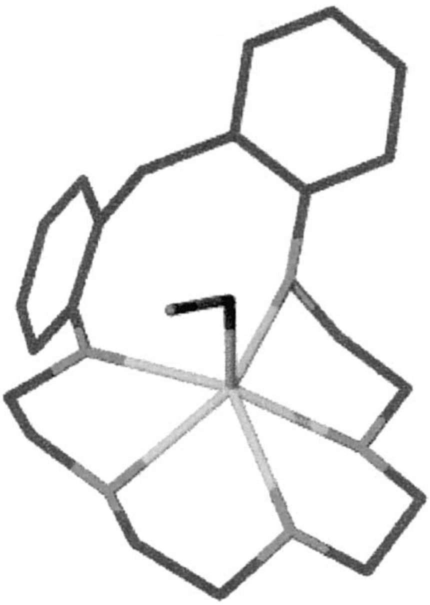


Fig. 35. NaNCS complex of 18-O_5-(2,2′)-diphenylmethano-2_4-coronand-5 showing the strained eight-membered chelate ring.

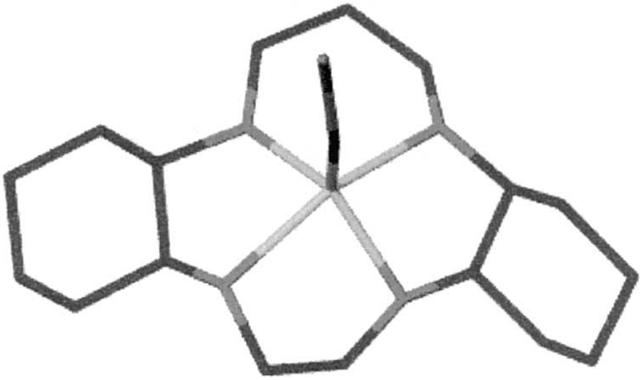


Fig. 36. Lithium complex of dicyclohexyl-13-crown-4 [90].

3.1. Complexes of Li^+

The small size of Li^+ means that other ligands are frequently incorporated into Li^+ crown ether structures, usually simultaneously coordinated to the metal cation and hydrogen bonded to the crown ether. The crown ether thus acts as both a first- and second-sphere ligand for the alkali metal cation. A particularly striking

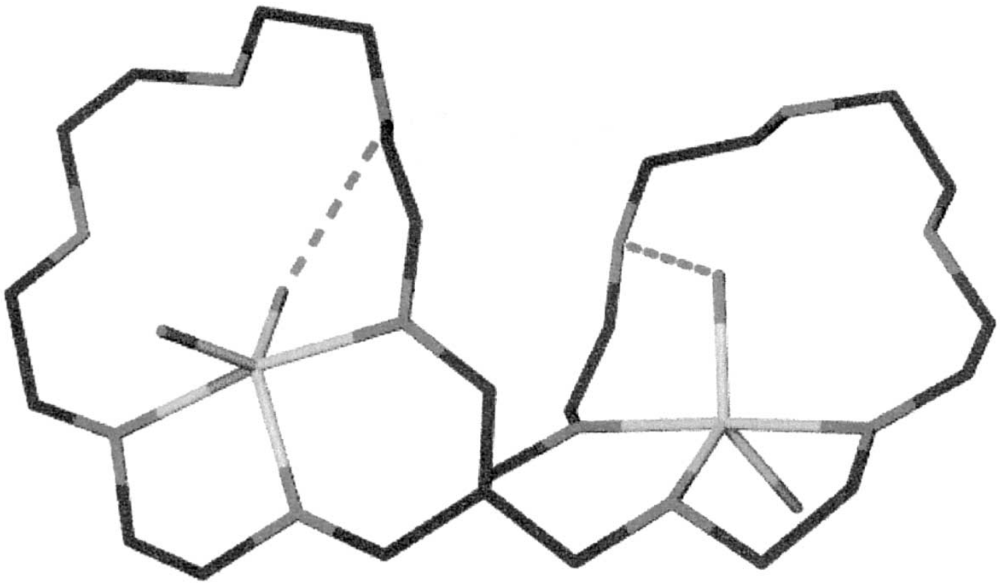


Fig. 37. 18,18′-Spiro-bis(19-crown-6) bis(lithium) diiodide tetrahydrate. Note the position of the Li^+ ions close to the C_3 spacer forming a six-membered chelate ring [91].

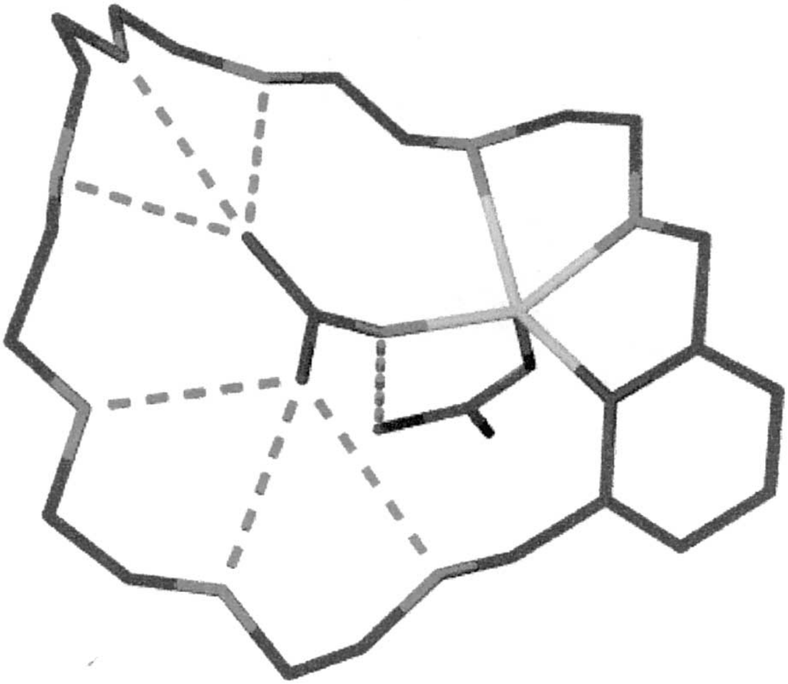
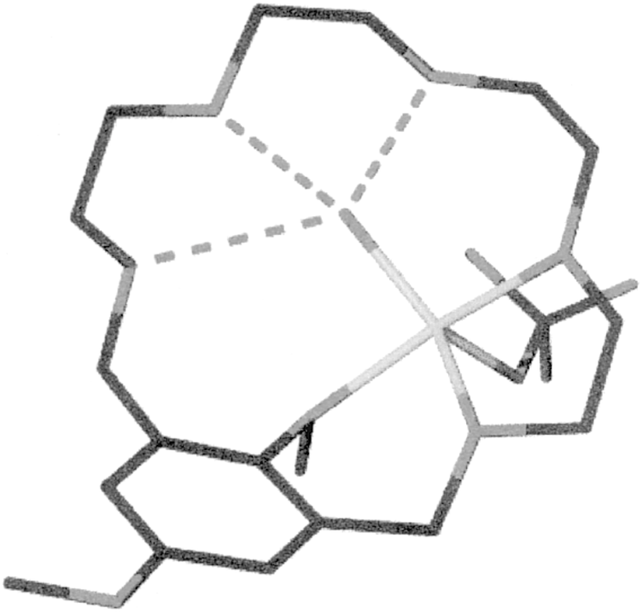


Fig. 38. Simultaneous first and second sphere coordination of Li^+ by 2,6-pyrido-27-crown-9. The second sphere coordination is via hydrogen bonds to the coordinated urea molecules. Hydrogen bonded N···O distances are in the range 2.875–3.168 Å [98].

example concerns $[Li(urea)_2(2,6\text{-pyrido-27-crown-9-N,O})](ClO_4)$ in which the small Li^+ ion occupies one side of the huge crown ether, coordinating to just two crown ether oxygen atoms and the pyridyl nitrogen as well as two O-bound urea molecules. The remainder of the crown ether is engaged in hydrogen bonding with the urea NH_2 functionalities, Fig. 38 [98]. Water is a much more common hydrogen bond donor than urea, however, and second sphere complexes of hydrated Li^+ are extremely common. A related example to **21** is the lithium perchlorate complex of the 1,4-dimethoxybenzene-derived 18-membered crown ether **22**, Fig. 39 [99]. This complex involves the formation of one normal and one bifurcated hydrogen bond thus allowing both water protons and all three available crown ether oxygen atoms to become involved in hydrogen bonding interactions. Perhaps the most elegant example of this phenomenon is the simple 18-crown-6 complex $[Li(H_2O)_2(18\text{-crown-}6)](ClO_4)$ (**23**) in which the Li^+ ion is situated far to one side of a symmetrical D_{3d} 18-crown-6 host. The two lithium-coordinated water molecules form an O–Li–O angle of 110.09° thus orientating one proton each towards the opposite side of the crown ether, resulting in the formation of a symmetrical pair of hydrogen bonds with O···O distances of 2.85–2.88 Å, Fig. 40 [100]. Similar effects are seen for the structure of **21** (Fig. 37) and even the incorporation of two Li^+ ions in the 1:2

complex of LiBr and LiCl with 18-crown-6 is not sufficient to obviate the need of additional stabilising hydrogen bonding interactions to coordinated water [101].



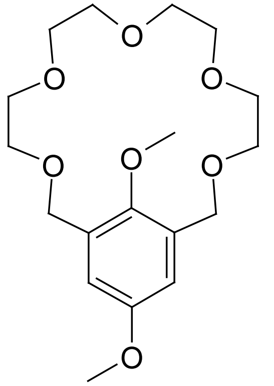


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Fig. 39. Simultaneous coordination of crown ether **22** to Li^+ and Li^+-bound water. Two of the three hydrogen bonding interactions are significantly longer than the third indicting bifurcation [99].

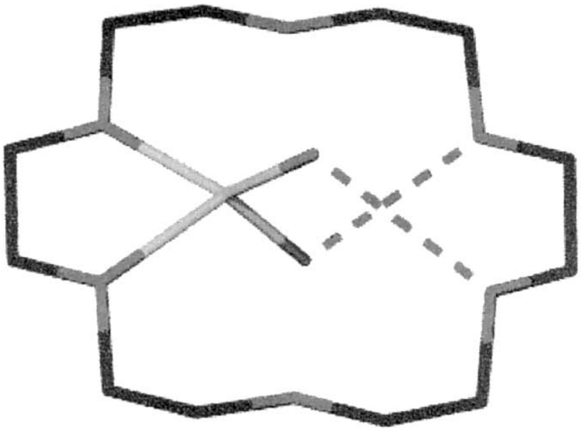


Fig. 40. Hydrogen bonding of two coordinated water molecules to $[Li(18\text{-crown-}6)]^+$ [100].

3.2. Complexes of Na^+

Junk and Steed and co-workers have carried out a thorough examination of the role of hydrogen bonding interactions in hydrated Na^+ complexes of 18-crown-6 [56]. As with **23** similar dihydrates are seen for sodium complexes of non-coordinating anions such as N_3^-. In the case of $[Na(H_2O)_2(18\text{-crown-6})](N_3)$ (**24**) the larger Na^+ ion extends further into the 18-crown-6 cavity than in **23** interacting with four crown ether oxygen atoms, though two at one end of the cavity much more closely than the central pair. The O–Na–O angle formed by the aqua ligands is expanded to 131.5° (from 110.07° for **23**) and hydrogen bonded O···O distances are 2.88 Å. The conformation of the crown ether possesses exact crystallographic symmetry, resulting in an interesting twofold disorder of the entire $Na(H_2O)_2^+$ unit. In the presence of oxygen donor anions such as NO_3^-, ClO_4^- and ReO_4^- that coordinate to the Na^+ ion, monohydrate structures are obtained. In each case the Na^+ ion is situated to one side of the crown ether interacting with four to five crown oxygen atoms and the complexes exhibit varying degrees of $OH_2 \cdots O_{crown}$ hydrogen bonding, the most significant being in the case of $[Na(H_2O)(NO_3)(18\text{-crown-6})]$ (**25**), Fig. 41. The crown conformation is apparently kinked upwards at the non-coordinating oxygen atoms to take advantage of the O–H···O hydrogen bond although this effect is apparently dependent on the presence of complementary intramolecular $C–H \cdots O_{nitrate}$ interactions. Remarkably the structure of the $AgNO_3$ analogue is essentially identical [102] highlighting the dominance of size dependent ion-dipole and hydrogen bonding interactions in these systems (the ionic radius of Ag^+ is comparable with that of Na^+). In the case of the ReO_4^- complex the crown ether relaxes back to its more common D_{3d} conformation. Most remarkable is the structure of the methanol complex $[Na(MeOH)_2(18\text{-crown-6})](BPh_4)$ (**26**) which exhibits a remarkable crown ether conformation clearly optimised for the short

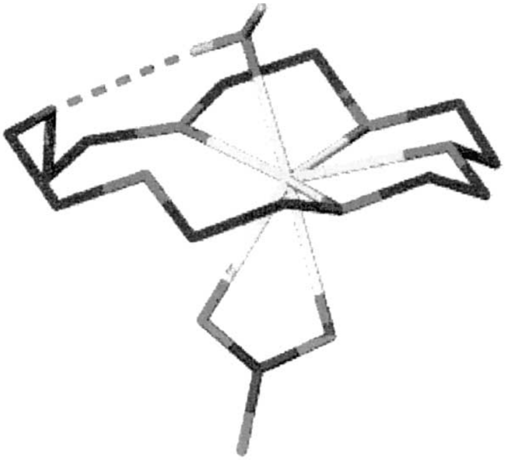


Fig. 41. Intramolecular hydrogen bonding in $[Na(H_2O)(NO_3)(18\text{-crown-6})]$ **25** [56].

(2.786 Å) $OH\cdots O_{crown}$ hydrogen bond, Fig. 42 [103]. In aqueous media reaction of $NaBPh_4$ with 18-crown-6 results in the formation of two forms of hydrogen bonded $[Na_2(H_2O)_3(18\text{-crown-}6)_2]^{2+}$ species reported independently by Steed [56] and Ng [104].

These results contrast with the much earlier structure of $[Na(H_2O)(18\text{-crown-}6)]SCN$ in which the crown ether adopts a most interesting distortion involving the movement of one crown oxygen to an axial position of the Na^+ ion while the remaining five surround the equator [59]. The other axial site is occupied by a coordinated water molecule, however, the wrapping conformation of the crown ether means that it is not available to act as a hydrogen bond acceptor and both aqua protons interact with the SCN anion, Fig. 43. Conversely the analogous I_3^- dihydrate structure adopts yet another coordination mode in which the Na^+ cation is situated more symmetrically in the macrocycle cavity while the linear O–Na–O vector lies at an angle of 72° with respect to the crown ether plane in order to maximise both intra- and intermolecular $O–H\cdots O_{crown}$ interactions. A similar structure is observed for $[Na(H_2O)_2(18\text{-crown-}6)][Fe(N_3)_2(TPP)]$ (**27**) (TPP = tetraphenylporphyrinato dianion) in which there exists simultaneous intermolecular hydrogen bonding to the coordinated azido anions and intramolecular interaction to the crown ether, Fig. 44 [105]. Also closely related is the Na^+ complex of tetraphenyl-18-crown-6 in which intermolecular hydrogen bonds are to CH_2Cl_2 molecules [106].

An entirely different situation is encountered, however, as soon as a second, uncomplexed crown ether is present to act as a hydrogen bond acceptor. In the case of $[Na(H_2O)_2(18\text{-crown-}6)][PtCl_4(glycyl)]\cdot 18\text{-crown-}6$ (**28**) the uncoordinated crown ether acts solely as a second sphere ligand to the Na^+ ion, by hydrogen bonding to coordinated water resulting in the formation of a hydrogen bonded polymer, while the other crown ether acts solely as a first sphere ligand (Section 4.2) [107]. A qualitatively similar situation is encountered for the methanol solvate of sodium dibenzo-18-crown-6 in the presence of free dibenzo-18-crown-6 and $W_6O_{19}^{2-}$ [108].

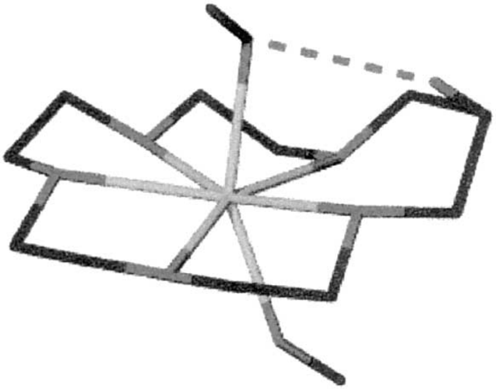


Fig. 42. Strong intramolecular hydrogen bonding in complex $[Na(MeOH)_2(18\text{-crown-}6)](BPh_4)$ **26** [103].

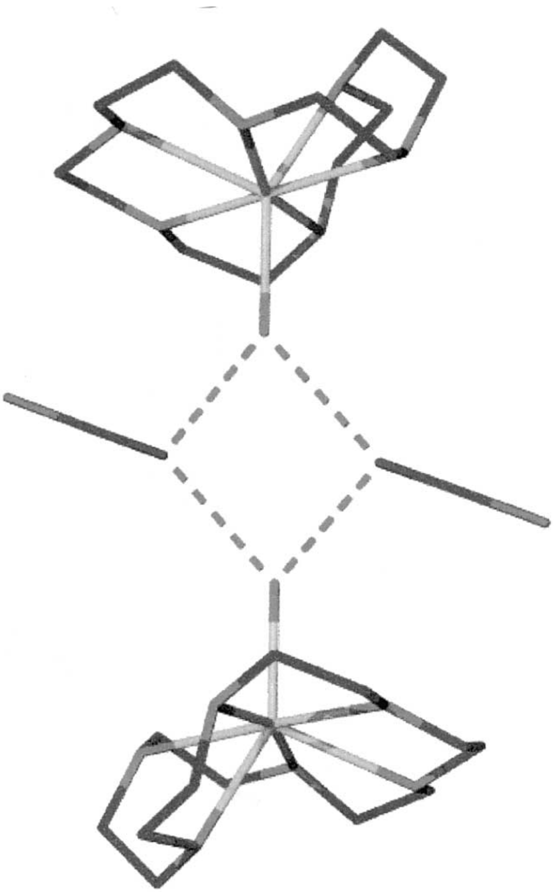


Fig. 43. Axial deformation of 18-crown-6 that results in an absence of 'intramolecular' hydrogen bonds in [Na(H_2O)(18-crown-6)]SCN [59].

Similarly, when the crown ether is too small to allow simultaneous coordination and hydrogen bonding, intermolecular hydrogen bonds to anions or other species are observed. Thus, [Na(H_2O)(15-crown-5)] exhibits two hydrogen bonds to the chloride ligands of the $[Au_3Cl_3(StBu)]^-$ anion in the complex formed between them [109].

3.3. Complexes of K^+ Rb^+ and Cs^+

Larger ions such as K^+ and Rb^+ generally do not allow sufficient flexibility in their complexes with smaller crown ethers to enable the crown ligand to simultaneously act as a first and second sphere ligand to a single metal ion. As a result complicated structures can result as the system attempts to satisfy the hydrogen bonding requirements to coordinated water. In the complex [K(H_2O)(18-crown-

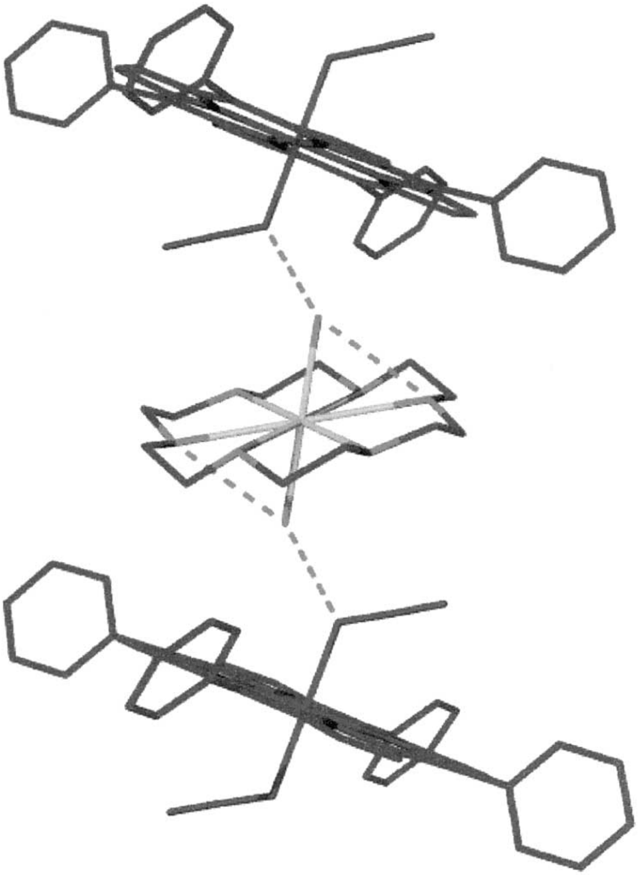


Fig. 44. Simultaneous intermolecular hydrogen bonding to the coordinated azido anions and intramolecular interaction to the crown ether in $[Na(H_2O)_2(18\text{-crown-}6)][Fe(N_3)_2(TPP)]$ **27** [105].

6)][K(18-crown-6)][$Cr(NCS)_5(H_2O)$]·H_2O (**29**) the K^+ coordinated water molecule is hydrogen bonded to the sulfur atom of an NCS^- ligand that is, in turn coordinated to chromium(III) via its nitrogen atom and the second (non-hydrated) potassium ion by its sulfur terminus. Thus the water molecule acts as a first sphere ligand for K^+ and a second sphere ligand for both K^+ and Cr^{3+}. The lattice water molecule, while uncoordinated to any metal ions, is hydrogen bonded to one of the crown ether ligands and to the chromium-coordinated water ligand, Fig. 45 [110]. The 18-crown-6 complex of potassium azide represents an interesting contrast to the Na^+ analogue (**24**) since the softer potassium coordinates directly to the azide anion to give a sunrise type complex $[K(H_2O)(N_3)(18\text{-crown-}6)]$ (**30**). As with **24** the coordinated water molecule is able to act as both a first and second sphere ligand to the K^+ ion via hydrogen bonding. However, it is the azide anion rather than the crown ether that acts as the acceptor, reflecting the much more limited geometric

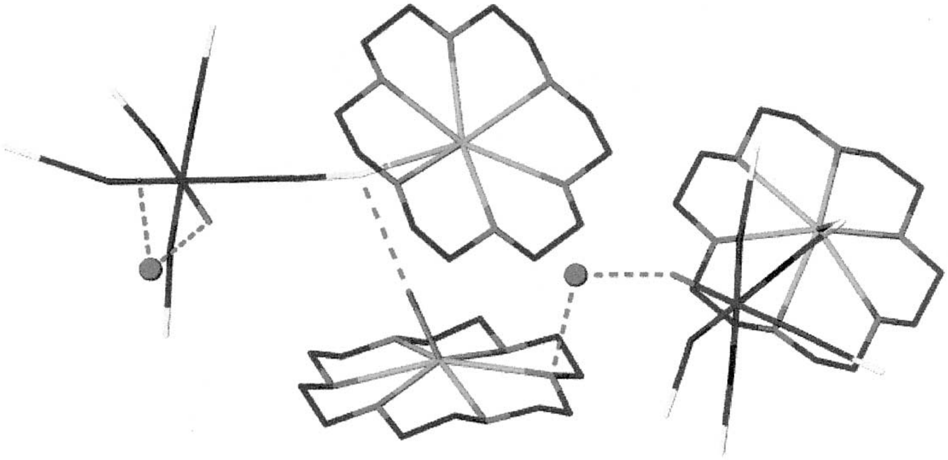


Fig. 45. Hydrogen bonding in [K(H_2O)(18-crown-6)][K(18-crown-6)][Cr($NCS)_5$(H_2O)]·H_2O **29** [110]. Spheres represent uncoordinated water molecules.

freedom in the K(18-crown-6)$^+$ unit, Fig. 46 [111]. Remarkably, however, simultaneous first and second sphere coordination of 18-crown-6 to K$^+$ is possible, as long as the mediating first sphere 'ligand' is large enough to allow sufficient flexibility, thus K$^+$ is able to sit unsymmetrically within an elliptically distorted 18-crown-6 cavity in [K(18-crown-6){$PtCl_5$(H_2O)}] (**31**). The K$^+$ ion forms four short K–O_{crown} interactions (ca. 2.75 Å) and two longer bonds with oxygen atoms on opposite sides of the crown ring. These more distant oxygen atoms act as acceptors for intra- and intermolecular hydrogen bonds from the Pt(IV) coordinated water molecule, Fig. 47 [112]. The K$^+$ ion fits within the macrocyclic cavity without any sunrise type doming. Clearly, however, with any smaller ligands, intramolecular interactions are not geometrically feasible and in cases such as the *iso*-propanol complex **12** intermolecular hydrogen bonding to the anions is encountered [47].

Increasing the size of the metal ion still further to Rb$^+$ removes ligands on the 'domed' face of the metal ion even further from the oxygen acceptors of coordinated 18-crown-6. However, Rb$^+$ is sufficiently large that coordination of water may occur on the concave face of the complex as well, bringing the solvent molecule into close proximity with the coordinated crown ether oxygen atoms, as in diaqua-(18-crown-6)-(hydrogen isonitrosocyanoacetamide)-rubidium isonitrosocyanoacetamide monohydrate (**32**), Fig. 48 [113]. Not only is the crown ether involved in first and second sphere coordination to the same Rb$^+$ ion, but there is a third sphere interaction as well, via a molecule of lattice water. The acetamide functionalities also engage and simultaneous first and second sphere coordination. Complex **32** in particular highlights the synergistic interplay between coordination and hydrogen bonded interactions in these versatile and malleable systems. Similarly, if flexibility is provided by substituting the crown ether, then intramolecular second sphere interactions are entirely feasible, as in the Cs$^+$ complex of 18-crown-6-2-carboxylato-3,8,9,14,15-pentacarboxylic acid, Fig. 49 [114].

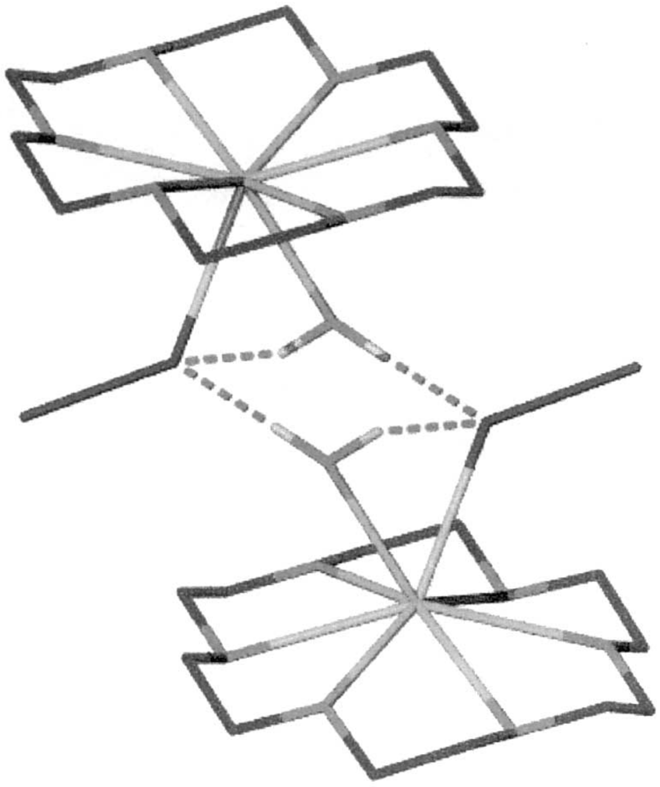


Fig. 46. Hydrogen bonding to coordinated N_3^- in $[K(H_2O)(N_3)(18\text{-crown-6})]$ **30**.

4. Second- and third-sphere coordination

4.1. Double shell clathrates

Double shell clathrates represent a large family of general formula $[(M^{II}X_4)\{M^I(18\text{-crown-6})\}_4](TlX_4)_2$ ($M^I = Rb$, Tl; $M^{II} = Zn$, Cu, Mn, Co; $X = Cl$, Br) [115]. The term double shell comes from the fact that the guest anion, MX_4^{2-}, occupies a lattice cavity surrounded by a tetrahedral sheath of $[M(18\text{-crown-6})]^+$ which is in turn surrounded by a framework of TlX_4^- anions, held together by long range X···X interactions. Thus, formally, the crown ether ligands act as third sphere ligands for the M^{II} cation. The structure of $[(MnBr_4)\{K(18\text{-crown-6})\}_4](TlBr_4)_2$ (**33**) is shown in Fig. 50. In this case Br···Br interactions are of the order of 4.0 Å, while $MnBr_4$–K^+ distances are 3.83 Å [116]. Using a smaller combination, $[Na(15\text{-crown-5})]^+$ an analogous complex $[(Br)\{Na(15\text{-crown-5})\}_4](TlBr_4)_2$ (**34**) can be prepared in which the double shell cavity encapsulates a single bromide anion, Na–Br distance 2.889 Å [117]. The group of Domasevitch have also recently reported an 'empty cavity' double shell clathrate $NH_4TlI_4{\cdot}2(18\text{-crown-6}){\cdot}NH_3$ in

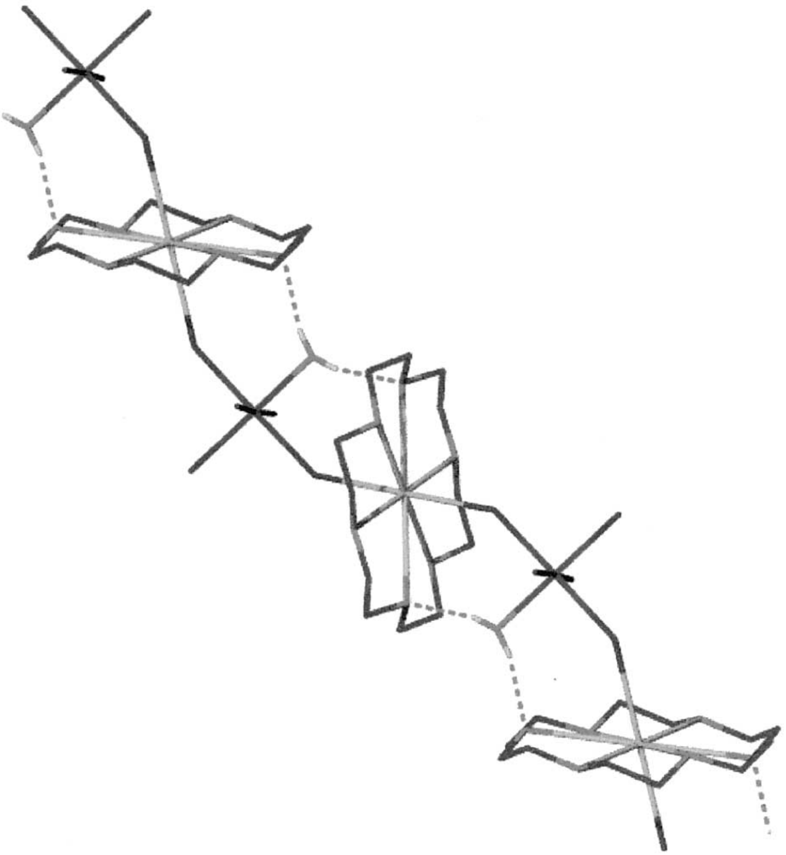


Fig. 47. Simultaneous first and second sphere coordination of 18-crown-6 to K^+ via a $[PtCl_5(H_2O)]^-$ 'ligand' in **31** [112].

which the role of M^I is taken by a pair of ammonium ions and two ammonia molecules [115].

4.2. Hydrogen bonded chains

There exists a large body of work on crown ethers as second sphere ligands for transition metal complexes as well as lanthanides and actinide aqua species [52,96,97,118–134]. The vast majority of such species are infinite hydrogen bonded chain structures, although some discrete oligomeric species are known [95,135–138]. In general d and f block complexes are outside of the scope of this review although three examples serve to illustrate the variety of such structures. In the case of $[La(NO_3)_3(H_2O)_2(1,10\text{-phenanthroline})]\cdot 15\text{-crown-5}$ a remarkable single helical chain is formed with a pitch of 43.77 Å comprising six lanthanum–crown pairs,

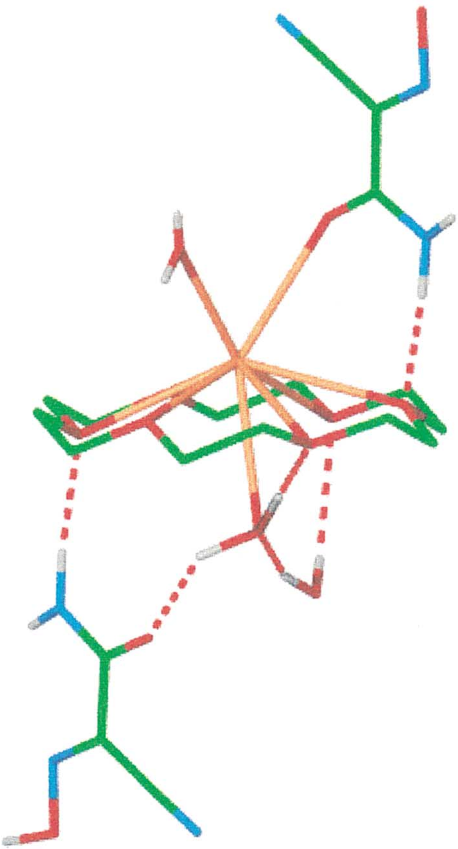


Fig. 48. 18-Crown-6 as part of a multiple coordination network in the Rb^+ species **32** [113].

hydrogen bonding via two coordinated water ligands, Fig. 51 [123]. Conversely, interaction of 15-crown-5 with $UO_2Cl_2(H_2O)_3$ results in a series of linear hydrogen bonded chains of alternating uranyl complexes and crown ethers again via hydrogen bonding to coordinated water. Interestingly however, intra- and inter-chain interactions result in the presence of sixteen crystallographically unique complex-crown pairs, Fig. 52 [118]. As an example of a network structure, reaction of H_2PtCl_6 with 18-crown-6 gives a variety of Pt(IV) oxonium-ion containing hydrates of which the most interesting is $(H_{13}O_6)[PtCl_5(H_2O)]\cdot 2(18\text{-crown-6})\cdot H_2O$ (**35**) [138]. This species contains a remarkable $H_{13}O_6^+$ oxonium ion encapsulated by hydrogen bonding within the cavity of three 18-crown-6 acceptors. One of the crown ethers also hydrogen bonds to the coordinated water molecule of the $[PtCl_5(H_2O)]^-$ anion both directly and via the intermediary of the lattice water molecule, Fig. 53. A particularly interesting recent example of crown ether second sphere coordination has been the use of crown ethers to stabilise ordinarily reactive species in ways that are normally associated with more encapsulating hosts such as cyclodextrins [139].

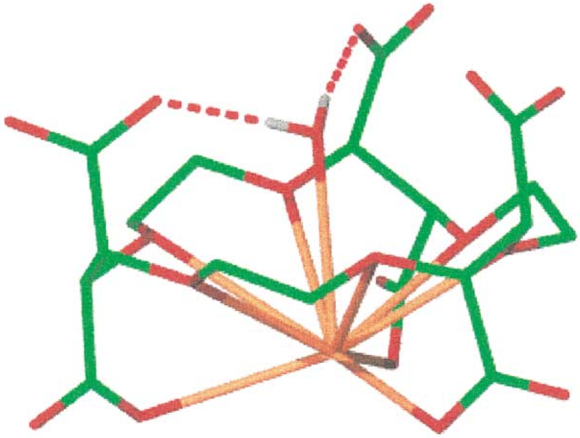


Fig. 49. First and second sphere coordination of 18-crown-6-2-carboxylato-3,8,9,14,15-pentacarboxylic acid to Cs^+ [114].

Thus, both 18-crown-6 and 15-crown-5 have been found to stabilise the normally reactive $[\{Fe(H_2O)_5\}_2(\mu\text{-}O)]^{4+}$ [133,140]. Second sphere hydrogen bonded interactions have also been found to have significant effects on molecular parameters as in the Cu–Cu distance $[Cu_2\{\mu_2\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ which contracts by some 0.3 Å from 2.827–2.862 in a number of examples containing limited intermolecular hydrogen bonding to 2.553 Å in $[Cu_2\{\mu_2\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]Cl_2.2(SC(NH_2)_2).2H_2O.2$(18-crown-6) [135].

In general such second sphere complexes tend not to be formed with alkali metal cations because of their relatively large size and low hydration energies, which usually results in direct crown ether coordination. Smaller, more highly charged main group metals, however, readily form linear chain structures such as $[Mg(H_2O)_5(NO_3)]NO_3\cdot$18-crown-6$\cdot H_2O$ (**36**) [141], Fig. 54. As the charge on the cation increases however, discrete complexes may form, with one face of the metal cation being occupied by interactions to the anions, while the other face is capped by hydrogen bonding to the crown ether. In the case of $[Al(H_2O)_6](NO_3)_3\cdot$18-crown-6 a hydrogen bonded dimeric structure is the result with pairs of $Al(H_2O)_6^{3+}$ units linked together by hydrogen bonds to NO_3^- anions [56].

Some examples do exist of crown ethers acting as second sphere ligands to alkali metal cations, however, these complexes generally also contain first sphere coordination of a second, independent crown ether. Thus, $[Li(H_2O)$(benzo-15-crown-5)$][Cu_4I_6]\cdot$benzo-15-crown-5 (**37**) exhibits a six coordinate Li^+ ion bound in a pentagonal pyramidal fashion with a basal crown ether and apical water molecule. The water is hydrogen bonded to the free crown ether which exhibits a very similar conformation to the complexed analogue, Fig. 55 [142]. The overall geometry of the bis(crown) complex is highly reminiscent of the analogous complex with $H_5O_2^+$ [95]. A sodium analogue is also known (in the presence of bis(2,3-dimercapto-2-butenedinitrile)-nickelate anion) but in this case the crown: cation stoichiometry is 3:2

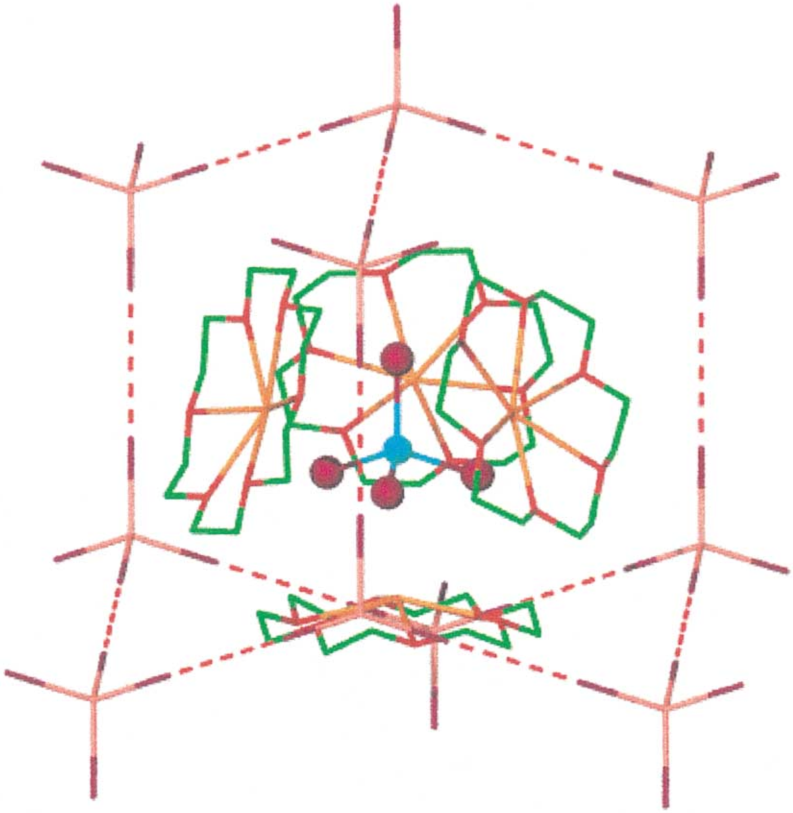


Fig. 50. Double shell clathrate structure of $[(MnBr_4)\{K(18\text{-crown-6})\}_4](TlBr_4)_2$ **33** [116].

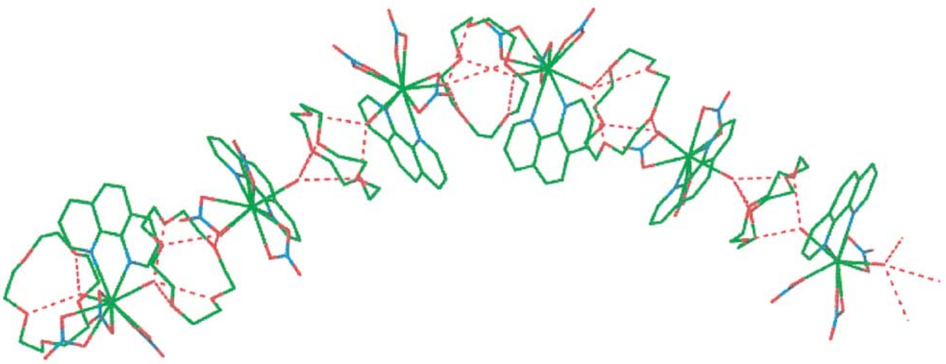


Fig. 51. Hydrogen bonded helix in $[La(NO_3)_3(H_2O)_2(1,10\text{-phenanthroline})]\cdot15\text{-crown-5}$ [123].

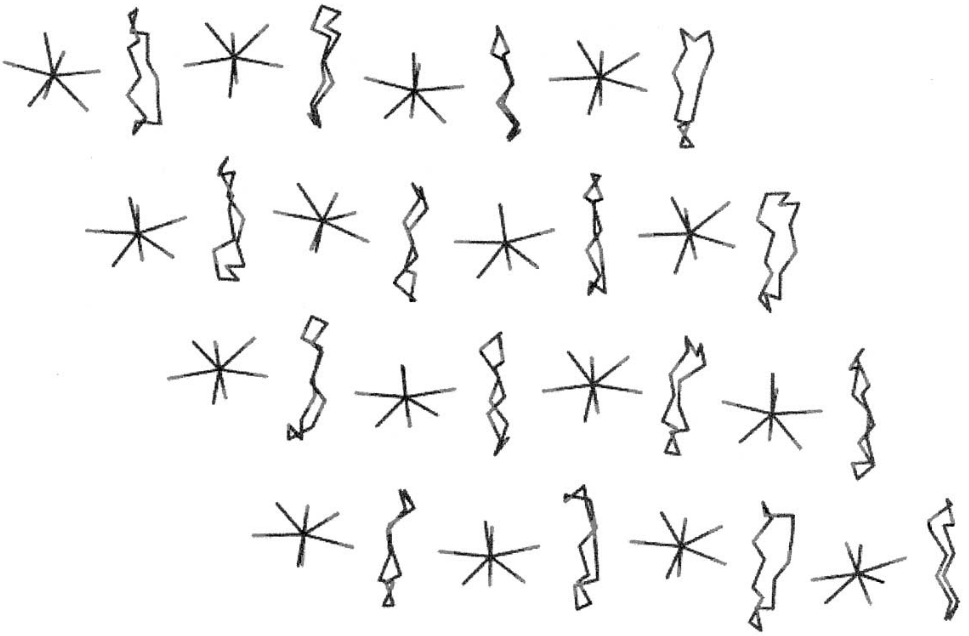


Fig. 52. Unique portion of the infinite linear hydrogen bonded chain structure of $[UO_2Cl_2(H_2O)_3]\cdot$15-crown-5 [118].

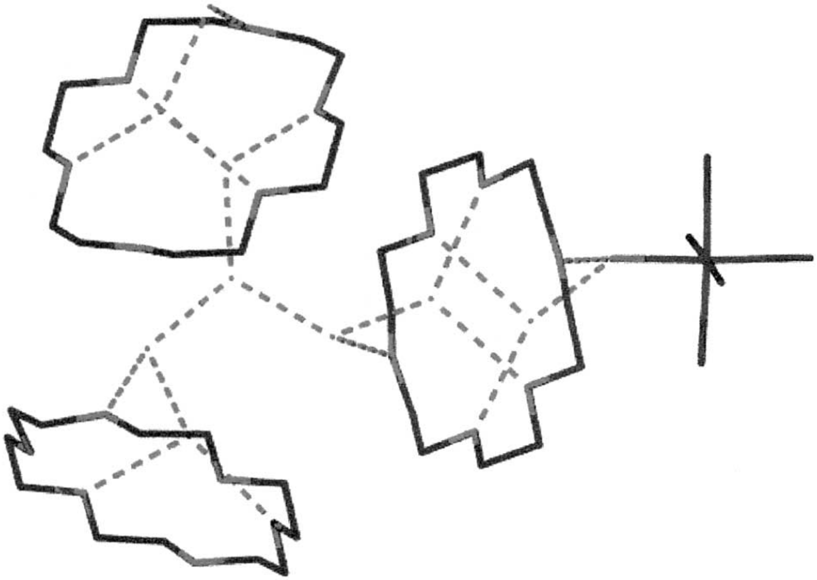


Fig. 53. The crown-encapsulated $H_{13}O_6^+$ ion in $(H_{13}O_6)[PtCl_5(H_2O)]\cdot 2(\text{18-crown-6})\cdot H_2O$ **35** [138].

with a single free benzo-15-crown-5 molecule acting as a second sphere ligand to both Na^+ ions via coordinated water [143]. This is particularly interesting given the unsymmetrical nature of 15-crown-5 which results in one face of the crown ether having two oxygen atoms available to act as hydrogen bond acceptors and the other face having three [97]. As a result one Na^+ aqua complex hydrogen bonds via

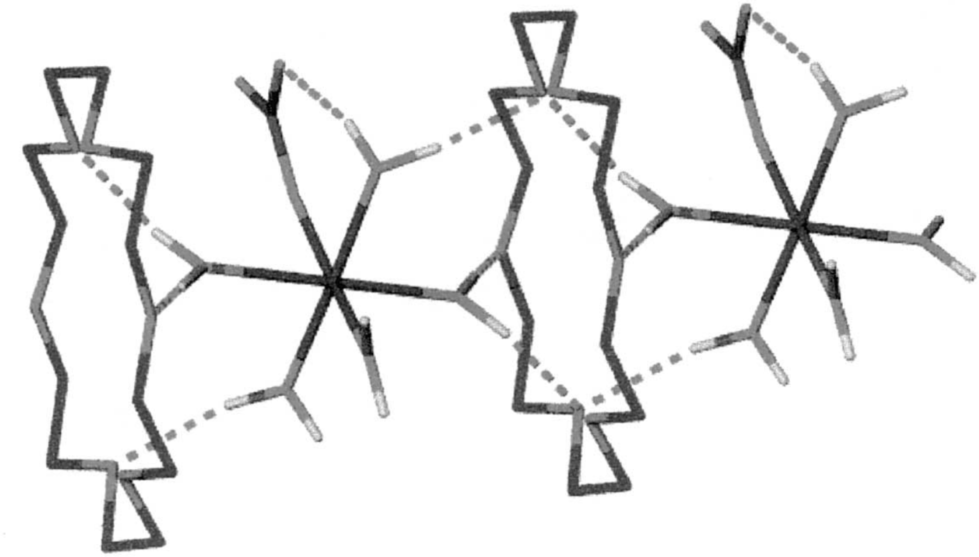


Fig. 54. Linear hydrogen bonded chain structure of $[Mg(H_2O)_5(NO_3)]NO_3 \cdot 18\text{-crown-}6 \cdot H_2O$ **36** [141].

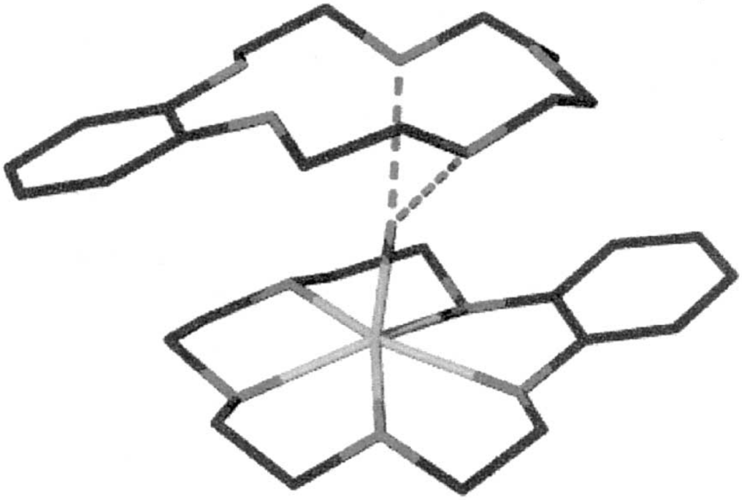


Fig. 55. Discrete $[Li(H_2O)(\text{benzo-15-crown-5})] \cdot \text{benzo-15-crown-5}$ unit in **37** [142].

two short interactions, whereas the other forms a single short bond and two longer, bifurcated interactions. Interestingly this 3:2 motif is also observed for Li^+ in the complex with bis((μ_4-bromo)-(12)mercuracarborand-4) [144]. In $[Na(H_2O)_2(18\text{-crown-}6)][PtCl_4(glycyl)]\cdot 18\text{-crown-}6$ (**28**) the uncoordinated 18-crown-6 adopts a cup-shaped conformation in order to hydrogen bond to one of the Na^+ coordinated water molecules on one face and the glycyl anion on the Pt(IV) complex on the other. The conformation of the hydrogen bonding crown ether is particularly important because of the obvious deviation from the usual D_{3d} symmetry, which allows the four oxygen atoms on one face to interact not only with the two glycyl NH protons but also to form supporting C–H···O hydrogen bonds to the adjacent methylene group, Fig. 56. A Pt-coordinated chloride ligand is hydrogen bonded to the remaining Na^+-bound aqua ligand, resulting in the formation of an infinite hydrogen bonded polymer in which a crown ether acts as a second sphere ligand for both Na^+ and Pt^{4+} [107]. In the methanol solvated sodium dibenzo-18-crown-6 complex with $W_6O_{19}^{2-}$ a free molecule of dibenzo-18-crown-6 is able to form part of an infinite hydrogen bonded chain via only two interactions to coordinated methanol, Fig. 57 [108]. However, in $[Na(H_2O)_2(18\text{-crown-}6)](CF_3SO_3)_2\cdot 18\text{-crown-}6$ the four water protons all interact with the free crown ether via four of the six oxygen atoms, resulting in an unusual ‘bottle’ shaped conformation, Fig. 58 [145].

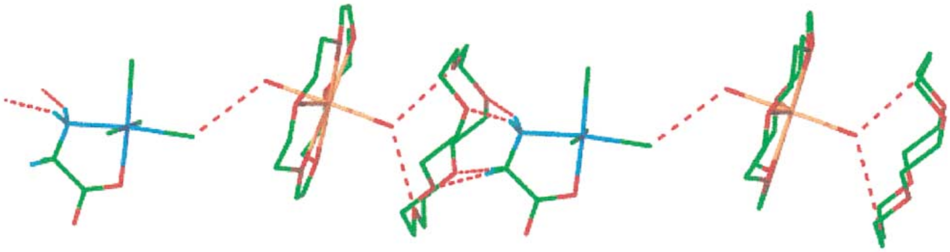


Fig. 56. Second sphere coordination of both Na^+ and Pt^{4+} by 18-crown-6. Note the CH···O hydrogen bonds [107].

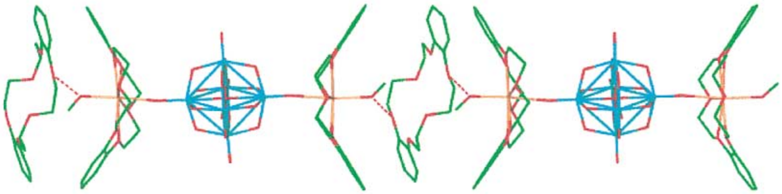


Fig. 57. Dibenzo-18-crown-6 accepting only two hydrogen bonds from Na^+ coordinated methanol [108].

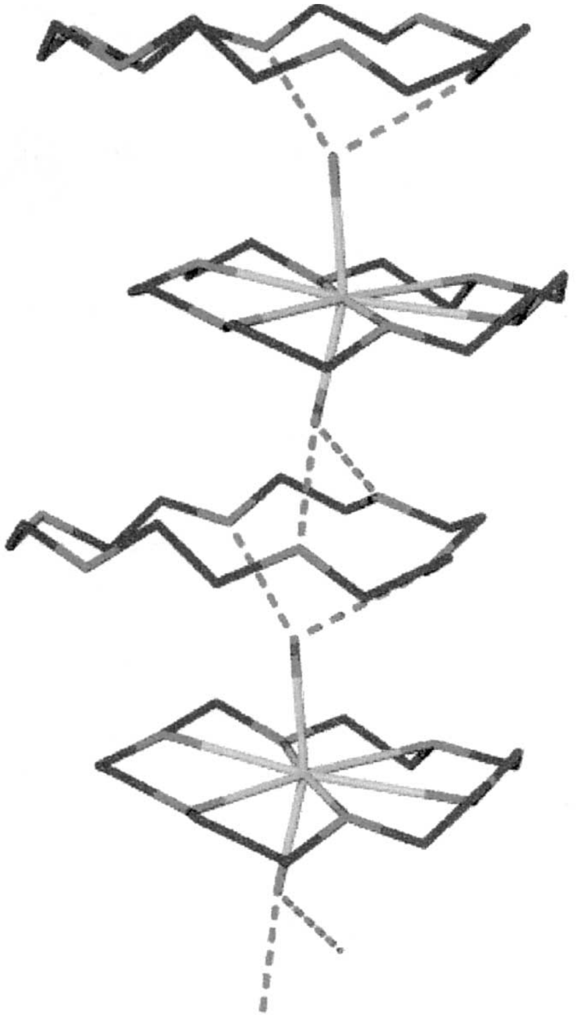


Fig. 58. 18-Crown-6 as a four-proton acceptor, resulting in a pinched 'bottle' shaped conformation [145].

4.3. Crown ethers as guest species (Matrioshka complexes)

Matrioshka are the traditional Russian wooden dolls which fit one inside the other. The term has been applied to compounds rather like the double shell clathrates in which an 'onion skin' like arrangement of hosts within hosts is encountered. In particular the quasi-spherical $[Li(12\text{-crown-}4)]^+$ cation may be incorporated as a guest within γ-cyclodextrin as part of a remarkable channel clathrate in which a repeating group of three cyclodextrin hosts includes alternating $[Li(12\text{-crown-}4)]^+$ cations and free 12-crown-4, Fig. 59 [146]. The uncoordinated crown ether probably hydrogen bonds with included water while, interestingly, the

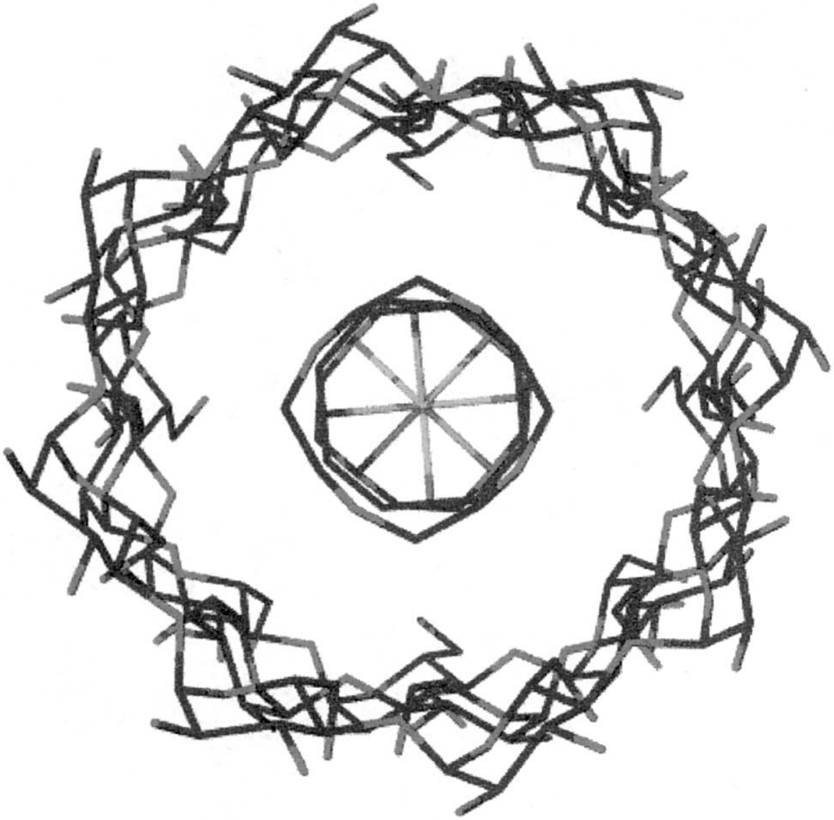


Fig. 59. Inclusion of 12-crown-4 and $[Li(12\text{-crown-}4)_2]^+$ within a tube of γ-cyclodextrin hosts [146].

Cl^- anion that balances the charge of the Li^+ containing cation is on the outside of the cyclodextrin. This represents a remarkable feat of charge separation (Li^+–Cl^- distance 11.48 Å).

A very different kind of Matrioshka complex has been reported recently by Raston et al involving the inclusion of alkali metal cation complexes of 18-crown-6 within a capsule formed by the face to face (upper rim) contact of two *p*-sulfonato-calix[4]arene anions. The structures are stabilised by the presence of large hydroxo-cations such as $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$, Fig. 60 [147]. Analogous ‘ferris wheel’ complexes containing only one calixarene have been with lanthanide crown ether cations [148]. Even more remarkably the same group has also prepared a complex in which a single $[(H_2O)_2(18\text{-crown-}6)]$ is encapsulated within a cage comprising six Ni(II) macrocycle dimers ($\{Ni(tmtaa)\}_2$, **38**) which act as divergent receptors, Fig. 61 [149].

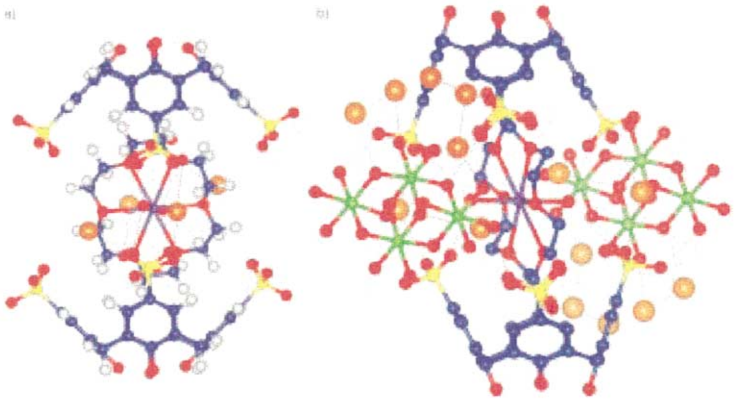
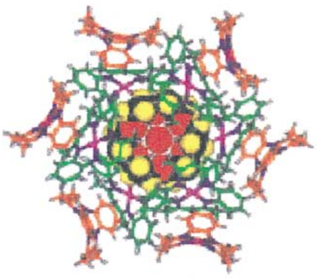
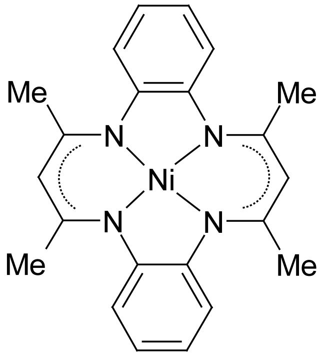


Fig. 60. Inclusion of $[Na(H_2O)_2(18\text{-crown-6})]^+$ within the cavity of two *p*-sulfonatocalix[4]arene hosts (reproduced with permission from Ref. [147]).





Ni(tmtaa) **38**

Fig. 61. $[(H_2O)_2(18\text{-crown-6})]$ encapsulkated by six Ni(II) macrocycle dimers of type **38** (reproduced with permission form Ref. [149]).

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