Crown ethers as stabilising ligands for oxonium ions†

Peter C. Junk

Received (in Durham, UK) 7th January 2008, Accepted 8th February 2008
First published as an Advance Article on the web 4th March 2008
DOI: 10.1039/b800122g

Oxonium ions ($H^+\cdot(H_2O)_n$) can be stabilised and isolated in the solid state by using crown ethers of differing sizes. Crown ethers can act as very good hydrogen bond acceptors for the binding of oxonium ions. It has been reasonably well established that 18C6 binds the H_3O^+ oxonium ion almost selectively in the cavity of the crown, while for the smaller crown ethers 12C4 and 15C5 the macrocycles generally span successive oxonium ions of varying nuclearity (H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$) to form hydrogen bonded polymers. Crown ethers larger than 18C6, *e.g.* 21C7 and 24C8 can bind $H_5O_2^+$ ions on the face of the crowns, while 30C10 appears to prefer two molecules of H_3O^+ in the cavity. It is the intention of this perspective to review the literature involving the solid state interactions of crown ether complexes involving oxonium ions.

1. Introduction

1.1 Oxonium ions

Acids have been variously defined over the past couple of hundred years. Pioneering work by Davy and Liebig found that some acids do not necessarily contain oxygen (*e.g.* HF, HCl and HBr) and an early definition claimed acids as "compounds containing hydrogen in which hydrogen can be replaced by a metal" implying they are a general class of hydrogen-containing compounds.[1,2] These observations countered Lavoisier's theory that acids were oxygen containing compounds.[2] It was recognised that these acids are associated with hydrogen atoms in an aqueous medium with Arrhenius and Ostwald's electrolytic dissociation theory.[1] As early as 1886, it was noted that water was essential for binary hydrogen compounds to perform as electrolytes.[2] Rutherford's identification of the proton, united these theories. It was realised that a particle of such a small size and high charge density should be closely associated with further electron density of other atoms and that an isolated proton was not expected to be a species to be found in high concentration.[3] In aqueous solution, it seemed reasonable to assume that according to an extension to Brønsted and Lowry's theory of acids and bases,[4,5] that water could act reasonably efficiently as a base and abstract a proton from an acid to yield H_3O^+. Solvent (H_2O) would not act independently of the system, and the nature of the hydration of the proton is generally not given (*e.g.* $H^+\cdot(H_2O)_n$, n not defined). The proton in aqueous solution was therefore assigned as an oxonium ion, H_3O^+. Hydronium is a common name for the H_3O^+ cation derived from the protonation of water. It is the simplest type of an oxonium ion. According to IUPAC nomenclature, the hydronium ion should be referred to as an oxonium ion. Hydroxonium has also been used unambiguously to identify this ion. An IUPAC proposal also recommends the use of oxonium and oxidanium in organic and inorganic chemistry, respectively. In this article the use of the terminology oxonium ion for any protonated water aggregate is adopted. The first report of the existence of H_3O^+ in the solid state was proposed by Volmer[6] where the similarity between the X-ray powder diffraction patterns of NH_4ClO_4 and $HClO_4\cdot H_2O$ were observed, and perchloric acid hydrate was inferred to be completely dissociated to H_3O^+ and ClO_4^-. A subsequent report on the ^1H NMR spectrum of hydrated perchloric acid demonstrated the equivalence of the protons, further suggesting the presence of H_3O^+.[7,8] The hydrates of nitric and sulfuric acids, ($HNO_3\cdot H_2O$ and $H_2SO_4\cdot H_2O$) also contained pyramidal shaped H_3O^+ ions (Fig. 1).[2]

It was not until the 1950s that the extent of hydration of the proton was more extensively studied.[9–11] These reports

Peter Junk graduated from The University of Western Australia in 1984 obtaining a BS in Physical and Inorganic Chemistry, and completed his PhD under the supervision of Professor Colin Raston in 1988. After four years employed in the petroleum industry, Peter held several Postdoctoral positions with the most relevant to this special edition being a two year stint with Prof. Jerry Atwood at the University of Alabama. Peter then gained an academic position at James Cook University as a Lecturer in Inorganic Chemistry and was given an accelerated promotion to Senior Lecturer in 1999. He moved to the School of Chemistry at Monash University in 2001 where he currently holds a position of Professor of Chemistry and is the Head of School. The leadership, mentoring and scholarship of Jerry Atwood has influenced Peter's career enormously, and he is indebted to Atwood for the opportunity to work with him between 1992 and 1994.

School of Chemistry, Monash University, Clayton, Vic., 3800, Australia. E-mail: peter.junk@sci.monash.edu.au; Fax: 61-3-9905 4597; Tel: 61-3-9905 4570

† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

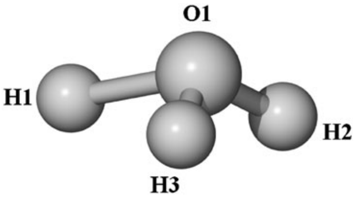

Fig. 1 Structure of pyramidal H_3O^+.

proposed an H_3O^+, surrounded by three hydrogen bonded water molecules bound in a first sphere fashion producing an $H_9O_4^+$ ion (Fig. 2). The outer water molecules can in turn hydrogen bond more weakly in second and third sphere fashions to extend the hydration of the proton. It is now well known that while the proton is usually simply inferred as H^+, the ion itself is always hydrated, as for most metal ions in solution, but the extent of hydration is variable and usually often dependent on the method of characterisation. It is also accepted that these hydrogen bonds are generally fluxional in solution, so identification of the degree of hydration of oxonium ions, can be very difficult. Several recent spectroscopic and theoretical considerations have reported on the nature of H_3O^+ in benzene and chlorinated hydrocarbon solvents,[12] and the structural isomerism of carbonic acid,[13] while the dynamics of a proton in aqueous solution have also been described using theoretical methods.[14] In the solid state however, this fluxionality is slowed down to such an extent, that the characterisation of these ions can be performed reasonably well using X-ray diffraction techniques, and nowadays, with CCD X-ray diffraction technology, these studies can be rapidly performed on very precise data. Thus, in the solid state, there have been many reports of oxonium ions $H^+\cdot(H_2O)_n$ where n can range from 1 to 6. In these systems, the reports of oxonium ions where $n = 1$ are rather numerous (>100). The first solid state report of the doubly hydrated proton appeared in 1967[13] and now there have been approximately 30 or so reports of this species, with the number of reports for higher oligomers decreasing rapidly with only a handful of structures for higher species where n is equal to or greater than 3.

In the solid state the structure of the H_3O^+ oxonium ion is, as expected, pyramidal (Fig. 1) as in isoelectronic NH_3, but the structure is a little more flattened with H–O–H angles varying considerably presumably due to extensive hydrogen bonding in many of these crystal structures. Thus the H–O–H angles in the monohydrates of HCl, (117°), HNO_3 (112°) and H_2SO_4, (101, 106 and 126°) have a wide range of variability. The solid-state structure of the $H_5O_2^+$ oxonium ion has been determined in a range of compounds and several different conformations have been established; (i) *cis*, linear, (ii) *trans*, linear and (iii) *gauche*, non-linear, (Fig. 3).[2] There are only relatively small energy barriers between these conformations, (*gauche* is approximately 2.5 kJ mol^{-1} more stable than *trans*, which itself in approximately 2.8 kJ mol^{-1} more stable than *cis*)[15] and the structure of the $H_5O_2^+$ ion isolated in the solid state is more often dictated by the potential hydrogen bonding environment of the oxonium ion. It can be difficult to determine the difference between a water molecule hydrogen bonded to an oxonium ion (*i.e.* $H_3O^+\cdot H_2O$) and a true $H_5O_2^+$ ion, but it has been proposed that in the $H_5O_2^+$ ion, the internal O–H distance must be greater than or equal to 1.10 Å and the O···O distance must be less than or equal to 2.48 Å, representing a very strong hydrogen bond.

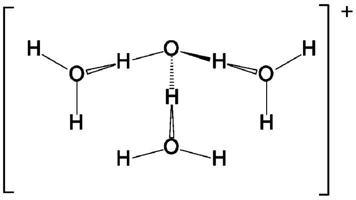

Fig. 2 Structure of pyramidal $H_9O_4^+$ with three water molecules hydrogen bonded to a central pyramidal H_3O^+.

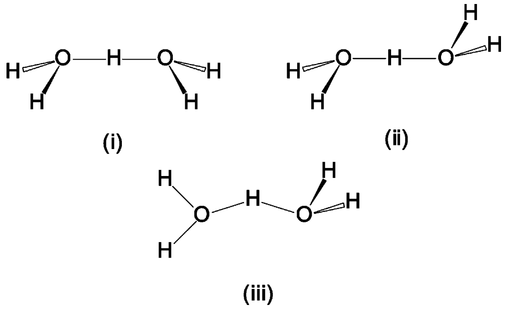

Fig. 3 Structures of the $H_5O_2^+$ ion: (i) *cis*, linear, (ii) *trans*, linear, and (iii) *gauche*, non-linear.

There are only about half a dozen $H_7O_3^+$ oxonium ions that have been structurally authenticated and these can be regarded as a bent molecule where an H_3O^+ ion is hydrogen bonded to two terminal water molecules. The angles about the central oxygen atom are similar to those for the H_3O^+ oxonium ion (105–116°[13]). The molecule is structurally asymmetric with the two O···O distances typically being in the order 2.45 and 2.55 Å. The $H_9O_4^+$ oxonium ion can be obtained as two different linkage isomers. In the first, the ion can be regarded as a pyramidal H_3O^+ with three terminally hydrogen bonded water molecules (alternatively, this ion can be viewed as an $H_7O_3^+$ ion with a further water molecule hydrogen bonded to the central H_3O^+). In the second, the ion exists as a chain type structure where an additional water molecule is hydrogen bound to the $H_7O_3^+$ ion in a linear fashion. The pyramidal structure has been calculated to be more stable by 19.7 kJ mol^{-1}. As with the smaller oxonium ions above, the structure of the oxonium ion is heavily dictated by the hydrogen bonding environment in which it exists.

Several higher oligomers of the $H^+\cdot(H_2O)_n$ series have been isolated, *e.g.* $H_{13}O_6^+$,[16] and $H_{14}O_6^{2+}$.[17] In the former, the $H_{13}O_6^+$ ion is involved in hydrogen bonding interactions and will be discussed below, however, the latter does not have any interactions with crown ethers.

1.2 Crown ethers

Crown ethers have been heavily investigated in research involving the host–guest chemistry of metal ions and neutral or ionic organic species since their discovery by Pedersen in 1967.[18,19] A number of previous reviews have appeared covering many aspects of their chemistry.[20–23] The selectivity of crown ethers for particular metal ions have been extensively studied and it has been suggested that ratios of cation radius to crown ether internal van der Waals diameter of 0.75–0.90 : 1 are suitable for metal ion encapsulation by the macrocycle.[24] Factors such as preorganisation and complementarity,[25] solvation and, significantly, chelate[26] have been accepted to be significant factors in the selectivity of the crown ethers for ions in solution. The conformational flexibility of crown ethers allows a variety of coordination environments in metal complexes and increases the solubility of ions in both aqueous and lipophilic media by exposing the hydrophilic (oxygen atoms) or hydrophobic (ethylenic groups) moieties of the molecule to solvent.

It is the intention of this review to discuss the interactions of oxonium ions with crown ethers. This area of chemistry is based on the premise that in order to isolate an oxonium ion as a stable entity, the cation must be involved in a hydrogen-bonded array with hydrogen bond acceptors. The crown ether family offer suitable binding pockets for oxonium ions but also can act as excellent hydrogen bond acceptors. Therefore, inclusion type complexes where the oxonium ions are totally bound by the crown ether (*i.e.* the size–fit and/or shape complementarity is perfect for this type of binding) are possible. It is also possible for the macrocycle to act as a bridging unit (hydrogen bond acceptor) in hydrogen bonded polymeric arrays of differing oligonuclearity where the size/fit of the oxonium ion to the crown ether is not suitable.

Table 1 Geometry of H_3O^+ ions encapsulated by 18C6 ligands (charges omitted on anions)

Compound	Geometry
$[H_3O^+\cdot 18C6(COOH)_4]$[29]	Pyramidal
$[H_2O\cdot 2,6\text{-pyrido-}18C6\cdot H^+][ClO_4]$[30]	Pyramidal
$[H_2O\cdot 2,6\text{-pyrido-}18C6\cdot H^+][\text{picrate}]$[30]	Pyramidal
$[H_3O^+\cdot 18C6]_2[Mo_6O_{19}]$[31]	Planar
$[H_3O^+\cdot 18C6][Cl–H–Cl]$[32]	Planar/pyramidal
$[H_3O^+\cdot \text{dicyclohexano-}18C6][Th(NO_3)_6]$[33]	Planar
$[H_3O^+\cdot 18C6]_2[Pd_2Cl_6]$[34]	Pyramidal
$[H_3O^+\cdot 18C6]_2[ZnCl_4]$[35]	Pyramidal
$[H_3O^+\cdot 18C6]_2[MnCl_4]$[35]	Pyramidal
$[H_3O^+\cdot 18C6][Br–H–Br]$[36]	Planar/pyramidal
$[H_3O^+\cdot 18C6][(H_5O_2{}^+)(Cl)_2]$[37]	Pyramidal
$[H_3O^+\cdot 18C6]_2[(UO_2(NO_3)_2C_2O_4]$[38]	Planar
$[H_3O^+\cdot 18C6][MoOCl_4(H_2O)]$[39]	Pyramidal
$[H_3O^+\cdot 18C6][ReOCl_4(H_2O)]$[39]	Pyramidal
$[H_3O^+\cdot 18C6]_2[FeCl_4]$[40]	Planar/pyramidal
$[H_3O^+\cdot 18C6][Br_3]$[41]	Planar
$[H_3O^+\cdot 18C6][I_7]$[42]	Planar
$[H_3O^+\cdot 18C6][CrCl_4(H_2O)_2]$[43]	Pyramidal
$[H_3O^+\cdot 18C6][(H_5O_2{}^+)Mo_2Cl_9]$[43]	Planar (pyramidal)
$[H_3O^+\cdot 18C6][WOCl_4(H_2O)]$[43]	Planar/pyramidal
$[H_3O^+\cdot 18C6][W(CO)_5Cl]$[44]	Pyramidal
$[H_3O^+\cdot 18C6][W(CO)_4Cl_3]$[44]	Planar
$[H_3O^+\cdot 18C6][MoOCl_4(H_2O)]$[45]	Pyramidal
$[H_3O^+\cdot 18C6][WOBr_4(H_2O)]$[45]	Planar
$[H_3O^+\cdot 18C6][TiCl_5(H_2O)]$[46]	Pyramidal
$[H_3O^+\cdot 18C6]_2[ReCl_6]$[47]	Pyramidal
$[H_3O^+\cdot 18C6][AuCl_4]$ (form I)[48]	Planar
$[H_3O^+\cdot 18C6][AuCl_4]$ (form II)[48]	Planar
$[H_3O^+\cdot 4\text{-nitrobenzo-}18C6][AuCl_4]$[48]	Planar
$[H_3O^+\cdot 18C6][NbF_6]$[49]	Planar
$[H_3O^+\cdot 18C6][TaF_6]$[49]	Planar

2. Crown ethers as binding agents for oxonium ions

2.1 [$H_3O^+\cdot$18C6] Complexes (18C6 = 18-crown-6)

18C6 has a perfectly suitable cavity for encapsulation of potassium ions in the solid state based on size of K^+ and the inner diameter of the macrocycle. Based on the same considerations, 15C5 is an excellent binder of sodium ions. The ionic radius of the H_3O^+ oxonium ion is midway between that of sodium and potassium ions, and therefore, these two crown ethers have been considered to be suitable binders for the simplest oxonium ion. However, other considerations need to be taken into account when predicting the binding capacity of crown ethers for these ions. Firstly, there is a symmetry match between H_3O^+ and 18C6 with each moiety having potential three-fold symmetry (see Fig. 4). For 15C5, no symmetry match is possible which may inhibit good binding capacity. Further, for an oxonium ion to reside at the centre of an 18C6 cavity, the $O_{(oxonium)}\cdots O_{(crown)}$ internuclear distances would be close to 2.8 Å; perfectly suitable for a hydrogen bonding distance for this ion (*cf.* O···O distances of 2.76 Å in ice).[27] In the smaller cavity of 15C5, these hydrogen bonding distances would have to be shorter if the ion were to reside within the macrocyclic cavity, therefore forcing the oxonium ion to reside outside one face of the cavity similar to some examples of the $[K^+\cdot 15C5]$[28] ion. Unsurprisingly, of all the

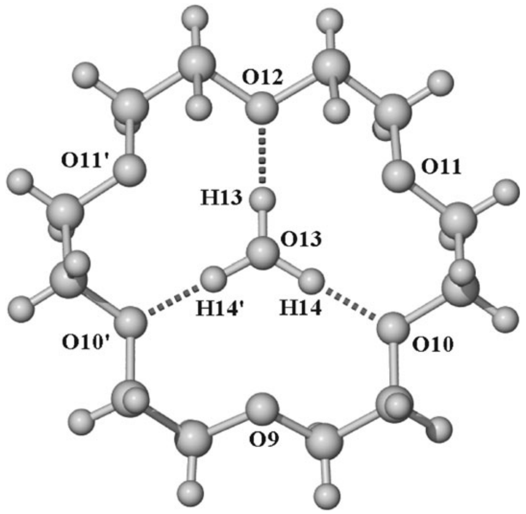

Fig. 4 X-Ray crystal structure of the $[H_3O^+\cdot(18C6)]$ cation showing the symmetry match of the H_3O^+ ion and 18C6 molecule.

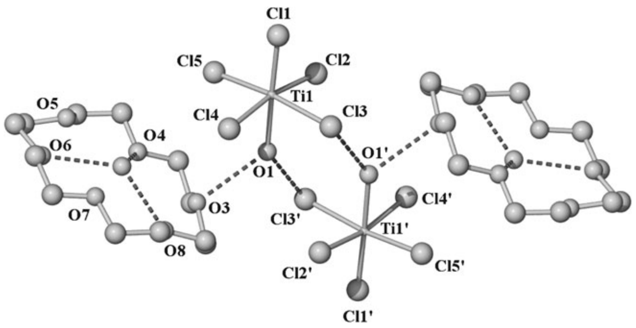

Fig. 5 X-Ray crystal structure of $[H_3O^+\cdot 18C6][TiCl_5(H_2O)]$ showing the hydrogen bonding between anions and cations.[46]

oxonium ions studied in the presence of 18C6 (see Table 1)[29–49] all but one of these have an H_3O^+ ion residing at the centre, or marginally to one side of the macrocyclic cavity. The first example of the $[H_3O^+\cdot 18C6]$ (Fig. 4) ion appeared in 1982 in $[H_3O^+\cdot$(tetracarboxylic-18C6)][Cl].[28] Since then there been many examples of the $[H_3O^+\cdot 18C6]$ cation published with complex anions such as $Mo_2Cl_9^{3-}$,[43] to the much more simple halide anions, such as Cl–H–Cl[32] and $[Br_3^-]$.[41] In most of these compounds, there is an extensive hydrogen bonding network involving anions, cations and water molecules (for example $[H_3O^+\cdot 18C6][TiCl_5(H_2O)]$ in Fig. 5).[46]

The geometric shape of the H_3O^+ oxonium ion when encapsulated within the 18C6 cavity has been the subject of many articles (Table 1).[29–49] For most of the information collated in Table 1 the structural work involving these species has been determined using X-ray crystallographic techniques, and only recently on more precise data collected on diffractometers with CCD detectors. Therefore, the location of the hydrogen atoms of the oxonium ions has not always been reliable, and the shape of the ion has been often inferred by considering the O···O vector as a close to linear hydrogen bond. To get unambiguous structural geometries of these ions, neutron diffraction studies will have to be performed. There are many reported examples of the oxonium ion in the expected pyramidal shape, for example in $[H_3O^+\cdot$18-crown-8][$ReOCl_4(H_2O)$][39] where the oxygen atom of the H_3O^+ ion resides 0.87 Å outside the plane defined by the crown ether oxygen atoms (Fig. 6). In this ion, the H–O–H angles are more obtuse than in an isolated H_3O^+ ion, presumably due to the hydrogen bonding between the ion and the oxygen atoms of the macrocycle which splays open the ion slightly. The ionic radius of the H_3O^+ ion is slightly smaller than the effective internal diameter of 18C6, the ion is forced into a more flattened conformation. In other examples, more planar shapes have been postulated for H_3O^+, *e.g.* $[H_3O^+\cdot 18C6]$[Cl–H–Cl] (Fig. 7) where the H_3O^+ oxygen atom is almost coplanar with the oxygen atoms of the crown ether (0.09 Å outside the plane defined by the closest three $O_{(crown)}$ atoms).[32] Here it was inferred that since the oxygen atom resides within the plane of the oxygen atoms, then the oxonium ion must necessarily be close to planar, if the O–H···O angle is close to linear. However, as mentioned earlier, in cases where the hydrogen atoms of the H_3O^+ ion are not located, presumably due either to the poor X-ray scattering ability of hydrogen atoms, or the potential disorder involving an H_3O^+ ion of three-fold symmetry residing in a macrocycle of six-fold symmetry, there is some doubt as to the overall shape of the ion. It is also possible that even though the oxygen resides within the plane of the crown ether oxygen atoms, the hydrogen atoms can be located out of this plane with an O–H···O angle <180°, while still maintaining a flattened pyramidal geometry for the oxonium ion.

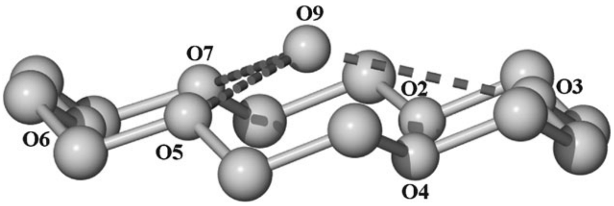

Fig. 6 Structure of the cation in $[H_3O^+\cdot 18C6][ReOCl_4(H_2O)]$ showing the $O_{(oxonium)}$ centre residing 0.87 Å out of the macrocycle.[39]

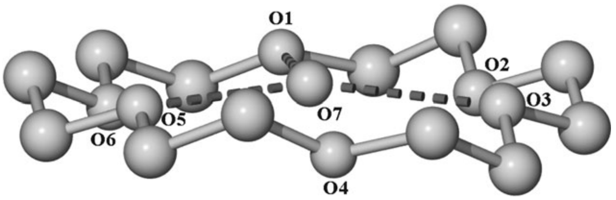

Fig. 7 Structure of the cation in $[H_3O^+\cdot 18C6]$[Cl–H–Cl] showing the $O_{(oxonium)}$ centre residing within the plane of the macrocycle.[32]

While the 18C6 macrocycle has shown a preference to bind H_3O^+ in the solid state, there are a number of examples in crown ether/oxonium ion chemistry where an oxonium ion of higher hydration (*e.g.* $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$) has been identified within the crystal lattice and with no interactions with the crown ether. In $(H_9O_4^+)[LaCl_2(H_2O)(18C6)]Cl_2$ a linear chain $H_9O_4^+$ ion is hydrogen bonded to the anions rather than the crown ether and the lanthanum atom is preferentially bound inside the macrocyclic cavity (Fig. 8).[50] In another rare earth complex, $(H_3O^+)[EuCl(H_2O)_2(18C6)]Cl_2$, the metal ion also resides within the macrocycle with the pyramidal oxonium ion in the lattice and hydrogen bonded to two chloride ions and a water molecule (Fig. 9).[50] The $O_{(oxonium)}\cdots O_{(water)}$ distance of 2.630(10) Å in this compound is too long for this fragment to be considered an $H_5O_2^+$ ion. These lattice-bound oxonium ions exist for several reasons; (i) due to strong hydrogen bonding acceptors/donors in the lattice, these species are stabilised with respect to loss of water, (ii) to balance the charge of complex anions, (iii) competition to accommodate the cavity of the crown ether between the metal ions (that are of a suitable size for complexation) and the H_3O^+ ion.

Even though it has been established that 18C6 is a very suitable encapsulator and binder of H_3O^+, particularly in the absence of metal ions that may otherwise compete for the macrocyclic cavity, there have been examples of higher oxonium ion oligomers isolated in the presence of this particular crown ether. There has been one report of an $H_5O_2^+$ ion bound to an 18C6 molecule in the unusual $[(H_5O_2^+)_2(18C6)][UO_2Cl_4]$.[38] In this complex, an $H_5O_2^+$ ion is hydrogen bonded to opposite faces of the crown ether in a *gauche* conformation. The $H_5O_2^+$ ions are then hydrogen bonded to the anions to form a polymeric strand (Fig. 10). The largest oxonium ion oligomer isolated in crown ether systems is the $H_{13}O_6^+$ ion. This is present in $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot(18C6)_2$ and is encapsulated in the lattice in a strongly hydrogen bonded system trapped between three 18C6 molecules as a linear $H_5O_{11}^+$ ion with a water molecule hydrogen bonded to the central O atom of the chain.[16] While the hydrogen atoms of the oxonium ion were not located, it is believed the ion exists as a $[H_3O\cdot H_2O\cdot H_2O(H_2O)\cdot H_2O\cdot H_2O]^+$ fragment based on O···O distances.

The ability of crown ethers to act as ion transporters for hydrophilic species across lipophilic regions has been extensively studied for the alkali metal ions. In a similar way, crown ethers can also impart hydrocarbon solubility to oxonium

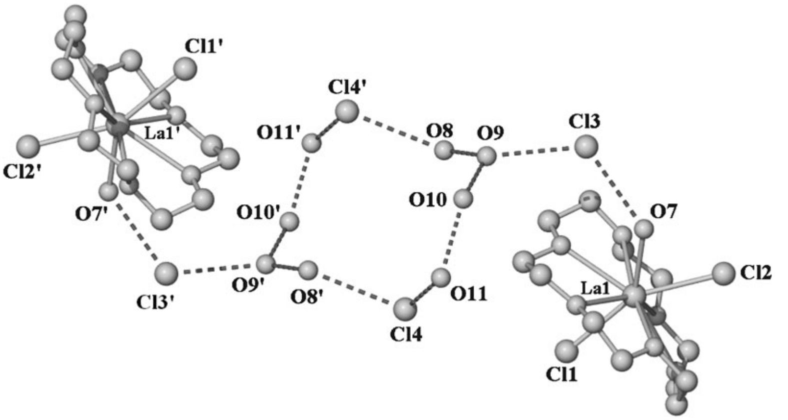

Fig. 8 X-Ray crystal structure of $[H_9O_4^+][LaCl_2(H_2O)(18C6)]Cl_2$ with a linear chain type of $H_9O_4^+$ ion.[49]

ions. To this end the liquid clathrate chemistry[51–53] of these species has been studied. In many of the complexes discussed above, oxonium ions have been found to crystallise from toluene, in which the liquid clathrate effect[51–53] as been observed. Also involved in a number of these species,[31,34,35,39,40,43–49] are transition metals which have potentially catalytic properties, so the possibility of studying catalysis in liquid clathrate media is an exciting prospect. The highly ionic medium and the potential for a simple separation mechanism[52,53] could have great merit.

2.2 21-Crown-7 (21C7), dicyclohexano-24-crown-8 (24-crown-8 = 24C8), dibenzo-24-crown-8 and dibenzo-30-crown-10 (30-crown-10 = 30C10)

Based on the affinity of 18C6 to selectively bind H_3O^+ ions in the solid state, it may be expected that macrocycles with cavities larger than that in 18C6 would bind larger oligomers in the $(H_2O)_n{\cdot}H^+$ oxonium ion series. There has only been one reported example of 21C7 and two examples of dicyclohexano-24C8 binding $H_5O_2^+$ ions,[54–56] and one involving dibenzo-24C8 while dibenzo-30C10 reportedly binds two ions of H_3O^+ within the cavity.[55] In this limited series, it is suggested that larger macrocycles do have the ability to stabilise the $H_5O_2^+$ ion, but that a threshold that is reached, where there is now competition between ability to stabilise the higher oligomers and the binding of several of the smaller H_3O^+ ions within the cavity.

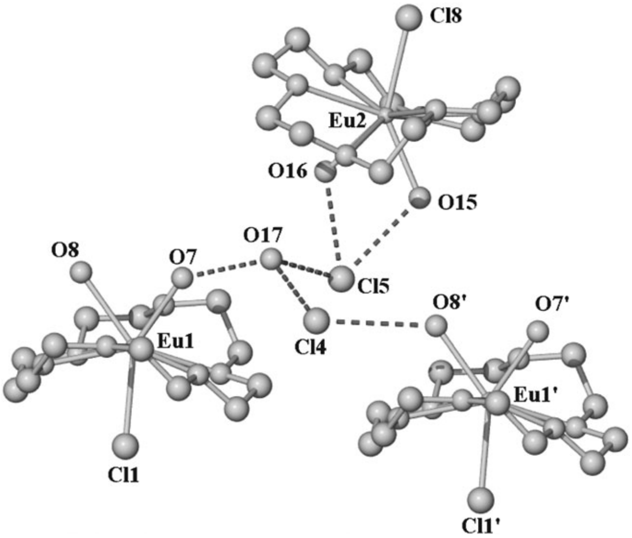

Fig. 9 X-Ray crystal structure of $[H_3O^+][EuCl(H_2O)_2(18C6)]Cl_2$ with a pyramidal H_3O^+ ion in the lattice.[49]

In $[H_5O_2^+{\cdot}21C7][WOCl_4(H_2O)]$,[54,55] the oxonium ion lies slightly outside the face of the macrocycle, and exists in the higher energy *cis* conformation (Fig. 11) suggesting the ion is a little too large for complete encapsulation within the cavity. Additionally, the mismatch of symmetry between the two species may also contribute to the offset location of the ion with respect to the crown ether. The O···O distance in the $H_5O_2^+$ ion of 2.41(3) Å is typical for these species. In $[(H_5O_2)(\text{dicyclohexano-24C8})]_2[UO_2Cl_4]{\cdot}MeOH$ and $[(H_5O_2)(\text{dicyclohexano-24C8})]_2[UCl_6]{\cdot}MeOH$ the *trans* $H_5O_2^+$ ion resides deep within the cavity, but here, the macrocycle appears to be slightly too large for the ion causing a folding of the ether to accommodate the hydrogen bonding requirements of the $H_5O_2^+$ ion (Fig. 12).[56] Other evidence that suggests the crown ether is slightly too large for this ion are the long $O_{(oxonium)}{\cdots}O_{(crown)}$ distances of 2.83(1) to 3.01(1) Å. The O···O distances in the disordered oxonium ions are 2.42(2) and 2.48(2) Å for the $UO_2Cl_4^{2-}$ species and 2.39(2) and 2.54(2) Å for the $[UCl_6]^{2-}$ complex.[56] Dibenzo-24C8 has been used to accommodate an $H_5O_2^+$ ion in $[H_5O_2^+{\cdot}\text{dibenzo-24C8}][AuCl_4]$ with the oxonium ion neatly embedded in the cavity of the crown ether.[48]

In the larger crown ether, dibenzo-30C10, there is the potential for complexation of higher oligomers of oxonium ions. The 30C10 molecule has a high conformational mobility, so it should be possible for the macrocycle to fold, and encapsulate $(H_2O)_n{\cdot}H^+$, where $n = 2$, 3 or 4, as in potassium ion complexes of dibenzo-30C10, where the K^+ ion is coordinated by all ten O(crown) atoms.[57,58] However, it was found that the dibenzo-30C10 macrocycle preferentially complexes two H_3O^+ oxonium ions, and adopts a much flatter conformation than in potassium complexes. The oxonium ions observed in $[(H_3O^+)_2(\text{dibenzo-30C10})][W(CO)_4Cl_3]_2{\cdot}(\text{toluene})_2$ and $[(H_3O^+)_2(\text{dibenzo-30C10})][WOCl_4(H_2O)]_2$ are the only compounds where complexation of H_3O^+ by dibenzo-30C10 are also first to exhibit a crown ether in which two oxonium ions are coordinated within the interior of the macrocycle. The crown ether adopts a relatively flat

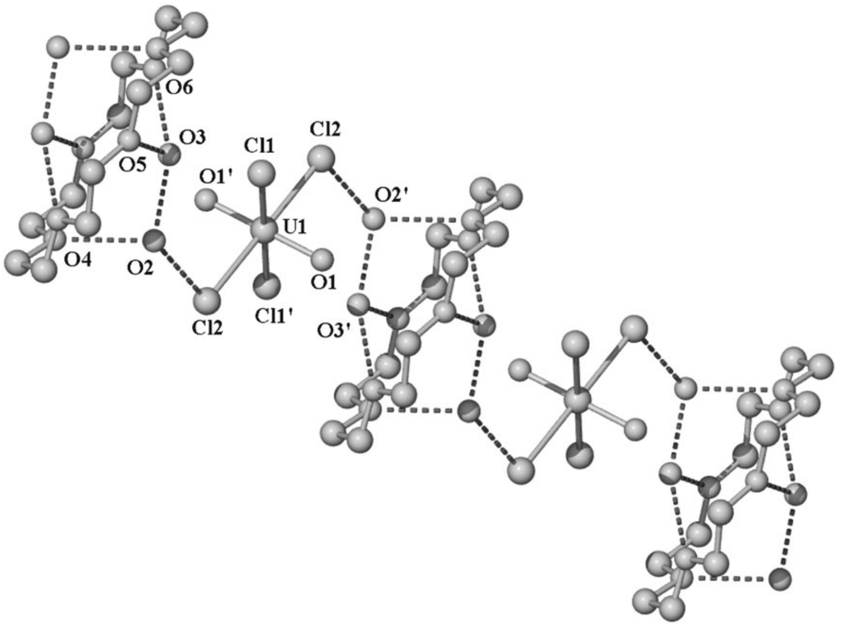

Fig. 10 X-Ray crystal structure of $[(H_5O_2^+)_2{\cdot}(18C6)][UO_2Cl_4]$ with an 18C6 molecule sandwiched between two $H_5O_2^+$ ions.[38]

conformation with an H_3O^+ oxonium ion bound toward either end of the cavity of the crown ether (Fig. 13). The oxygen atom of the oxonium ions reside approximately 0.3 Å out of the plane of the plane defined by the $O_{(crown)}$ atoms to which they are coordinated to, and have approximately pyramidal geometry. This type of geometry is the lowest energy conformation for the H_3O^+ ion, and is typically found in complexes where 18C6 has been used to selectively isolate H_3O^+, although there is some conjecture as to whether some of these complexes contain planar H_3O^+ ions (see above).[29–49]

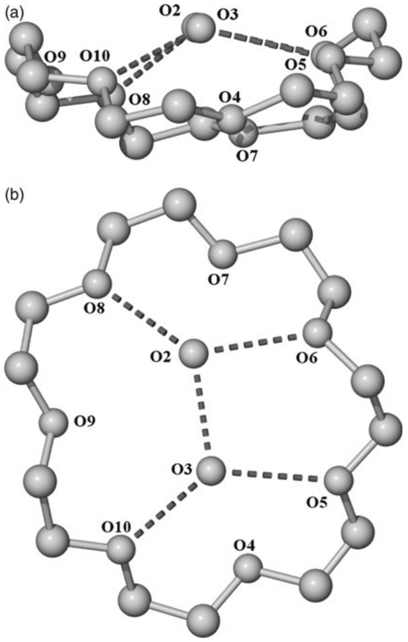

Fig. 11 X-Ray crystal structure of the cation in $[H_5O_2^+{\cdot}21C7]$-$[WOCl_4(H_2O)]$. (a) Projected along the O···O vector; and (b) onto the plane of the 21C7 macrocycle.[53,54]

2.3 12-Crown-4 (12C4) and 15-crown-5 (15C5)

As mentioned earlier, the smallest oxonium ion, H_3O^+, is approximately the same size as the cavity of 18C6 and therefore, based on size-fit arguments, there is little possibility of binding an H_3O^+ ion within the cavity crown ethers such as 12C4 or 15C5. The effective diameter of the cavity of the larger of these, 15C5,[59] is approximately 0.9 Å smaller than that of 18C6,[60] and suggests that an H_3O^+ ion will not fit in the interior of the crown. While the possibility of encapsulating an oxonium ion with 15C5 is all but eliminated, the crown can still act as a suitable hydrogen bond acceptor, setting up polymeric strands through successive oxonium ions and crown

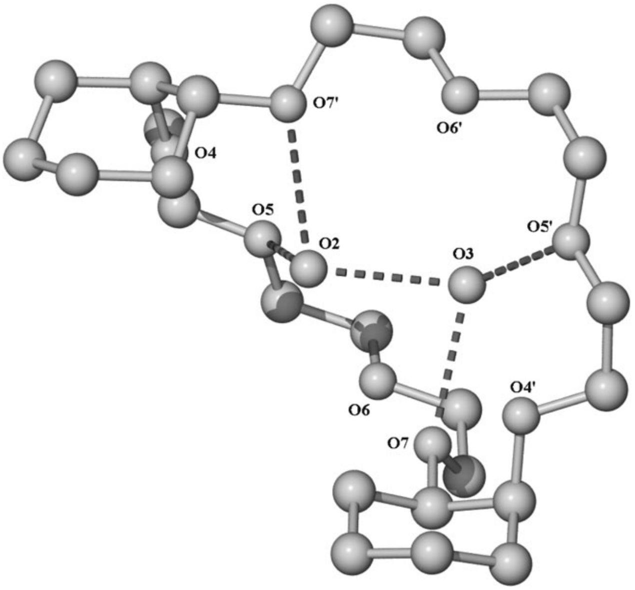

Fig. 12 X-Ray crystal structure of the cation in $[H_5O_2^+{\cdot}$(dibenzo-24C8][UCl_6)]·MeOH showing the $H_5O_2^+$ ion embedded deep within the cavity of the folded crown ether.[55]

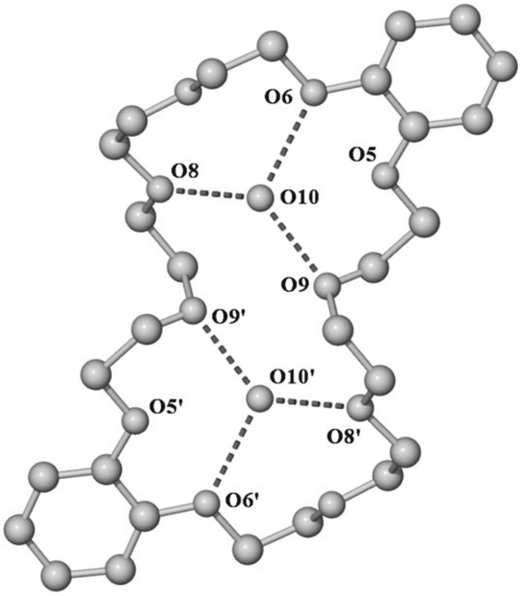

Fig. 13 X-Ray crystal structure of the cation in $[(H_3O^+)_2{\cdot}(dibenzo\text{-}30C10][WOCl_4(H_2O)]_2$ and $[(H_3O^+)_2{\cdot}(dibenzo\text{-}30C10][W(CO)_4Cl_3]_2(toluene)_2$.[54]

ether molecules (see later). There is also the possibility to form sandwich type structures where the two crown ethers bind an oxonium ion between them (*cf.* similar structures of $[K^+{\cdot}(15C5)_2])$.[61] These types of sandwiched species have generally been isolated with a *trans* $H_5O_2^+$ oxonium ion bound wedged between two 15C5 molecules (*e.g.* $[H_5O_2^+{\cdot}(15C5)_2][UO_2Cl_3(H_2O)_2]$[49,50,62]) or 12C4 (*e.g.* $[H_7O_3^+{\cdot}H_5O_2^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]$[63]) (Fig. 14 and 15). On the other hand, there is one example involving two 12C4 molecules with H_3O^+ filling the sandwich.[64] In the $H_5O_2^+$ oxonium ion in $[H_7O_3^+{\cdot}H_5O_2^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]_2$ the O···O separation of 2.327(8) Å is extremely short and is comparable with some of the shortest O–H···O hydrogen bonding distances known for example 2.34(1) Å in $[NEt_4^+]_3[H_5O_2^+][Mo_2Cl_8H][MoOCl_4(H_2O)]_2$.[65] O–H···O distances in $H_5O_2^+$ species are generally in the range 2.40–2.45 Å.[11] Compression of the $H_5O_2^+$ ion by the sandwiching effect of two 12C4 molecules presumably gives rise to the very short O···O separation in $[H_7O_3^+{\cdot}H_5O_2^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]_2$. Furthermore, the two 12C4 molecules of the sandwich are drawn together by hydrogen bonding involving the $H_7O_3^+$ oxonium ion which links successive $[H_5O_2^+{\cdot}(12C4)_2]$ fragments into a polymeric chain (Fig. 16, and below). The $O_{(oxonium)}{\cdots}O_{(crown)}$ distances in $[H_7O_3^+{\cdot}H_5O_2^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]$ are also relatively short indicating very strong hydrogen bonding between the units. In $[H_3O^+(12C4)_2][AsF_6]$, the H_3O^+ ion is bound between two 12C4 molecules as a discrete entity.[64]

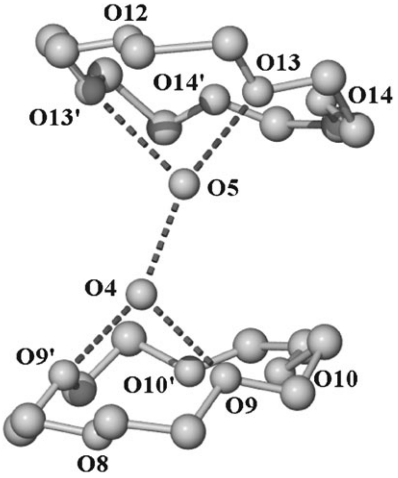

Fig. 14 X-Ray crystal structure of the cation in $[H_5O_2^+{\cdot}15C5][UO_2Cl_3(H2O)2)]$ showing the $H_5O_2^+$ sandwiched between two crown ether molecules.[49]

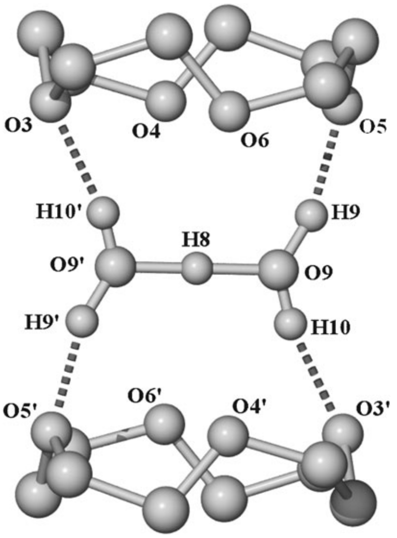

Fig. 15 X-Ray crystal structure of the $[H_5O_2^+{\cdot}(12C4)_2]$ fragment in $[H_7O_3^+{\cdot}H_5O_2^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]_2$.[62]

In systems involving transition metals, oxonium ions and crown ethers, the metal potentially competes with oxonium ions for coordination sites of the macrocycle. Metal complexation by a crown ether is possible if the ratio of the metal ion diameter to the crown cavity diameter, (*R*), falls within the range 0.75–0.90.[24] For first row transition metals, metal complexation is achievable for 15C5 (diameter, 1.7–2.2 Å[59]), but for 12C4 (diameter, 1.2–1.5 Å[59]) and 18C6 (diameter, 2.6–3.2 Å[60]) this does not typically occur and in the latter the crown ether can hydrogen bond in a second-sphere fashion to metal-coordinated water molecules, rather than being bound directly to the metal ion.[66] In examples involving 15C5, the metal can be bound within the macrocycle and oxonium ions reside within a hydrogen bonded array in the crystal lattice. In $[FeCl(H_2O){\cdot}15C5][H_5O_2^+][FeCl_4]$, and $[Co(H_2O){\cdot}15C5][H_9O_4^+][Co{\cdot}15C5][H_9O_4^+][Co(H_2O){\cdot}15C5][CoCl_4]_4$ the metal centres are encapsulated within the 15C5 molecule and water molecules or chloride ions bind in axial positions, forming seven-coordinate pentagonal bipyramidal structures with the crown ether in the five equatorial sites.[67] In $[FeCl(H_2O){\cdot}15C5][H_5O_2^+][FeCl_4]$ an $H_5O_2^+$ ion is hydrogen bonded between the cations and anions and forms a hydrogen bonded three dimensional array (Fig. 17). Emsley has stated that a hydrogen bond of >0.3 Å less than the sum of the van der Waals radii of the two elements, is classified a strong hydrogen

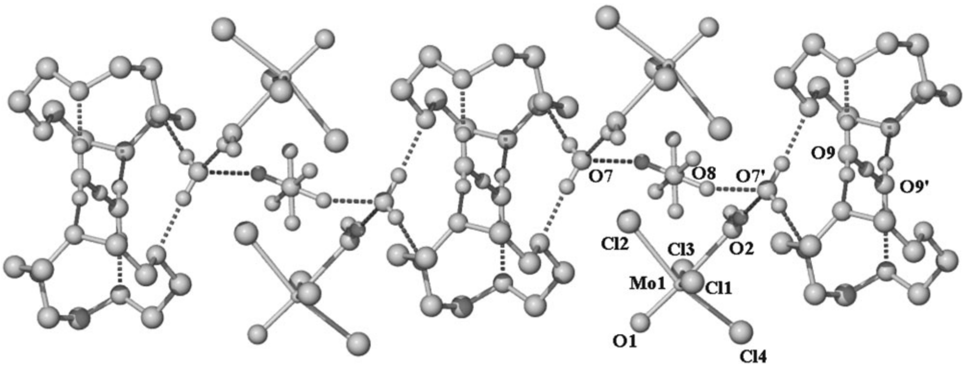

Fig. 16 X-Ray crystal structure of the $[H_7O_3{}^+{\cdot}H_5O_2{}^+{\cdot}(12C4)_2]_n$ polymeric chain in $[H_7O_3{}^+{\cdot}H_5O_2{}^+{\cdot}(12C4)_2][MoOCl_4(H_2O)]_2$.[62]

bond.[68] Here, the O···O internuclear distance of 2.337 Å is 0.46 Å less than the sum of the van der Waals radii for oxygen suggesting a strongly hydrogen bonded system.[69]

In $[Co(H_2O){\cdot}15C5][H_9O_4{}^+][Co{\cdot}15C5][H_9O_4{}^+][Co(H_2O){\cdot}15C5][CoCl_4]_4$ the water molecules in the axial positions of the *positively charged* cobalt atom are hydrogen bonded to a *cation*, H_3O^+, and further water molecules producing polymeric cationic strand involving $H_9O_4{}^+$ and Co^{2+} ions (Fig. 18).[67] In the linear-chain $H_9O_4{}^+$ ions, the central O···O distance of 3.036 Å precludes the $H_9O_4{}^+$ structure from being considered as an $H_5O_2{}^+$ ion with two terminally bound H_2O molecules as described for $[(H_5O_2{}^+)(H_9O_4{}^+)(benzo\text{-}15C5)2][UOCl_4]$.[38] Typical O···O separations in $H_5O_2{}^+$ ions range from 2.40–2.45 Å and in this $H_9O_4{}^+$ ion, the terminal O···O distances of 2.573 and 2.585 Å are short, almost suggestive of two $H_5O_2{}^+$ ions approaching each other. A further surprising feature of the short O···O distances in the terminal waters is the fact that they are bound to the positively charged Co^{2+} centre. In the uranium complex above, the corresponding terminal O···O distances are more conventional at 2.60 and 2.66 Å.[38]

There has been one reported example where an H_3O^+ ion is bound within an 18C6 molecule and an $H_5O_2{}^+$ ion resides within the hydrogen bonded lattice, *viz*. the triply chloro-bridged molybdenum dimer, $[H_3O^+{\cdot}18C6]_2[H_5O_2{}^+][Mo_2Cl_9]$. The structure involves the $H_5O_2{}^+$ ion hydrogen bonded to the anionic unit creating a $[H_5O_2{\cdot}Mo_2Cl_9]$ dianion. The O···O separation is 2.425(6).[43]

In $[(H_5O_2{}^+)(H_9O_4{}^+)(benzo\text{-}15C5)_2][UO_2Cl_4]$ the $H_5O_2{}^+$ ions are sandwiched between two benzo-15C5 molecules, and the linear chain $H_9O_4{}^+$ ions link these units to form a polymeric hydrogen bonded chain (Fig. 19).[38] Similarly, higher oligomers of oxonium ions have been isolated from liquid clathrates involving lanthanoid salts.[50,61] In $(H_5O_2{}^+)[UO_2(H_2O)_2Cl_3]{\cdot}(15C5)_2$ the $H_5O_2{}^+$ ions are sandwiched between the two 15C5 ions in the typical way. The $[UO_2(H_2O)_2Cl_3]^-$ anions link the sandwich units into polymeric strands through hydrogen bonding between the metal bound water molecules and the crown ether (Fig. 20).[50,61] In $[H_7O_3{}^+{\cdot}15C5][AuCl_4]$, the pyramidal shaped oxonium ion spans successive 15C5 molecules forming an infinite strand.[70]

There are many further examples where 12C4 binds with a range of oxonium ions $[H^+{\cdot}(H_2O)_n]$, $n = 1, 2$ and 3, and with the larger 15C5, an $H_5O_2{}^+$ ion has been identified to span successive crown ethers.[63,71] In these complexes, the oxonium ions, bind to the faces of the crown ethers, rather than being encapsulated by the macrocycle, and participate with other molecules in the crystal lattice to form hydrogen bonded networks.

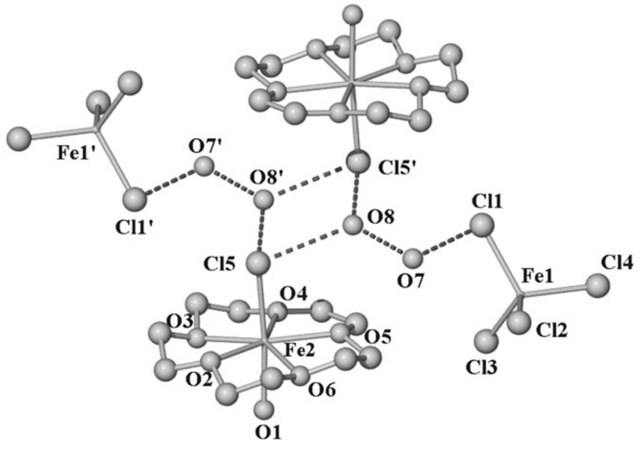

Fig. 17 X-Ray crystal structure of the hydrogen-bonded three-dimensional array in $[H_5O_2{}^+][FeCl(H_2O){\cdot}15C5][FeCl_4]$.[66]

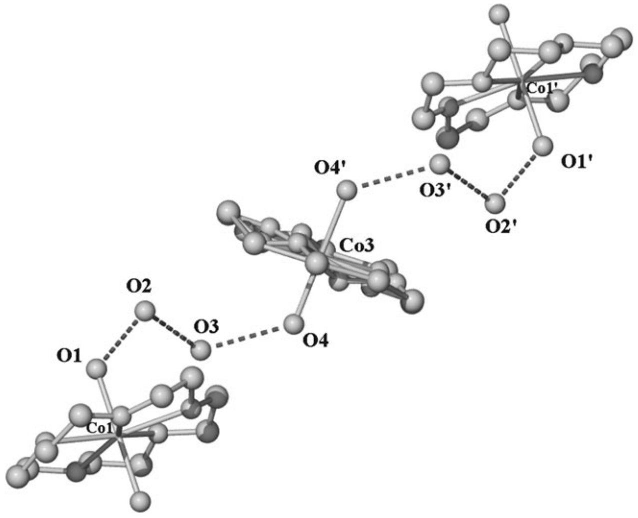

Fig. 18 X-Ray crystal structure of the $[Co(H_2O){\cdot}15C5][H_9O_4{}^+][Co{\cdot}15C5][H_9O_4{}^+][Co(H_2O){\cdot}15C5]$ oligomeric chain with linear chain-type $H_9O_4{}^+$ ions.[66]

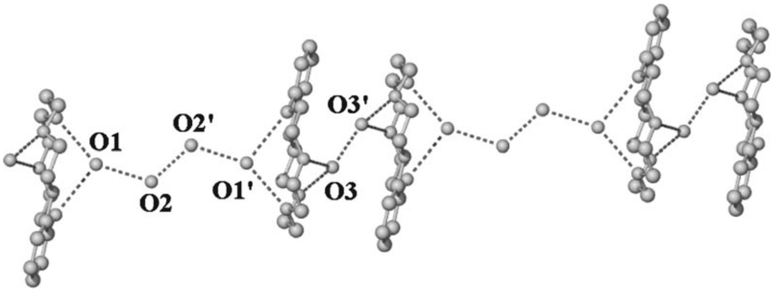

Fig. 19 X-Ray crystal structure of the {$[H_9O_4^+][H_5O_2^+ \cdot$(benzo-15C5)$_2$]} polymeric cationic chain in $[H_5O_2^+ \cdot H_9O_4^+ \cdot$(benzo-15C5)$_2$][$UO_2Cl_4$].[38]

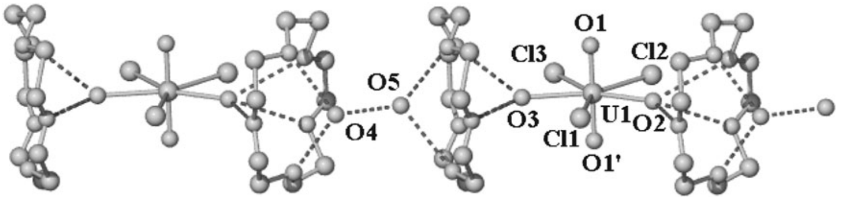

Fig. 20 X-Ray crystal structure of the polymeric chain in $[H_5O_2^+][UO_2(H_2O)_2Cl_3](15C5)_2$.[49,60]

In the complexes formed between 12C4 and oxonium ions, a variety of species have been isolated including H_3O^+, $H_5O_2^+$ and $H_7O_3^+$.[63] It is proposed that the larger oxonium ions form to link the 12C4 macrocycles into hydrogen bonded arrays at sufficient distance to generate pockets in which the large anions can reside.

The only oxonium ion identified in the structures of $[H_3O^+ \cdot 12C4]_3[Mo_2Cl_9]$ and $[H_3O^+ \cdot 12C4)][WOCl_4(H_2O)]$, was H_3O^+ where the O centre sits nearly 2.0 Å above of the face of the crown ether. The H_3O^+ ion is further involved in O–H···Cl hydrogen bonding with the anions in $[H_3O^+ \cdot 12C4]_3[Mo_2Cl_9]$ and $[H_3O^+ \cdot 12C4)][WOCl_4(H_2O)]$ (see for example Fig. 21).[63] In [(benzo-12C4)$_2 \cdot H_3O^+$][TaF_6], the oxonium ion is sandwiched between two 12C4 molecules rather than being involved in an extensive hydrogen bonding array with the anions.[49]

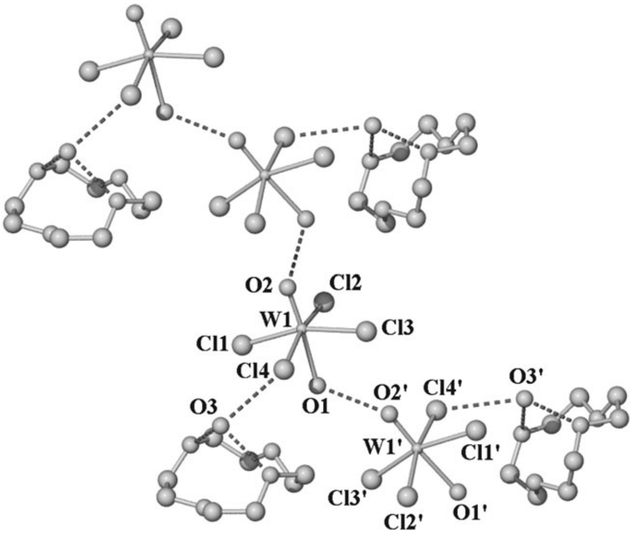

Fig. 21 X-Ray crystal structure of the polymeric chain in $[H_3O^+ \cdot 12C4][WOCl_4(H_2O)]$.[62]

The oxonium ions appear to be more strongly hydrogen bonded to the crown in $[H_3O^+ \cdot 12C4]$ complexes with O–H···O distances ranging from 2.488(5) to 2.531(5) Å which is much shorter than the related distances found in the 18C6 complexes above, where the typical values are 2.7–2.8 Å.[29–49] Short O–H···O distances are seen in $[H_3O^+][NO_3^-]$, $[H_3O^+][HSO_4^-]$ and $[H_3O^+]_2[SO_4]$ where the O···O separations are of the order 2.52–2.66 Å.[13] The reason for the formation of strong hydrogen bonds between the H_3O^+ oxonium ion and the 12C4 oxygen atoms is unknown. It may be that these are the expected O···O separations in these species and the related separations in the 18C6 complexes are long, due to the size of the macrocycle, but in the latter the hydrogen bonds are typical for OH···O bonds.

$[H_7O_3^+ \cdot H_5O_2^+ \cdot (12C4)_2][MoOCl_4(H_2O)]$ displays an example of a structure having *both* $H_5O_2^+$ and $H_7O_3^+$ in the same species (Fig. 16). It was the first reported instance of an $H_7O_3^+$ oxonium ion isolated from an aromatic medium.[63] In this structure the $H_7O_3^+$ ion resides on an inversion centre which creates a *linear and symmetrical* string of oxygen atoms, with O···O separations of 2.594(9) Å. The hydrogen atoms of the H_3O^+ at the heart of the $H_7O_3^+$ unit were not located due to conditional disorder of the H_3O^+ residing on an inversion centre. This example of a linear conformation for the $H_7O_3^+$ ion is unprecedented. $H_7O_3^+$ ions had previously been described as a central pyramidal H_3O^+ ion to which two H_2O molecules were hydrogen bound, with a O···O···O angle of *ca.* 115° and non-symmetrical O···O distances of 2.45 and 2.55 Å.[72] In $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12C4)_2][MoOCl_4(H_2O)]$ the $H_7O_3^+$ ion connects four 12C4 groups, with the terminal oxygen atoms of the $H_7O_3^+$ ion hydrogen bonded to the O atoms of the crown ethers at distances of 2.756(8) and 2.757(8) Å (Fig. 16). It was proposed that formation of the *linear* $H_7O_3^+$ ion was due packing constraints of the anions and cations in the crystal since the anions are also involved in hydrogen bonding with the $H_7O_3^+$ ion. The linear array for the $H_7O_3^+$ ions have not been considered by theoreticians but the energy

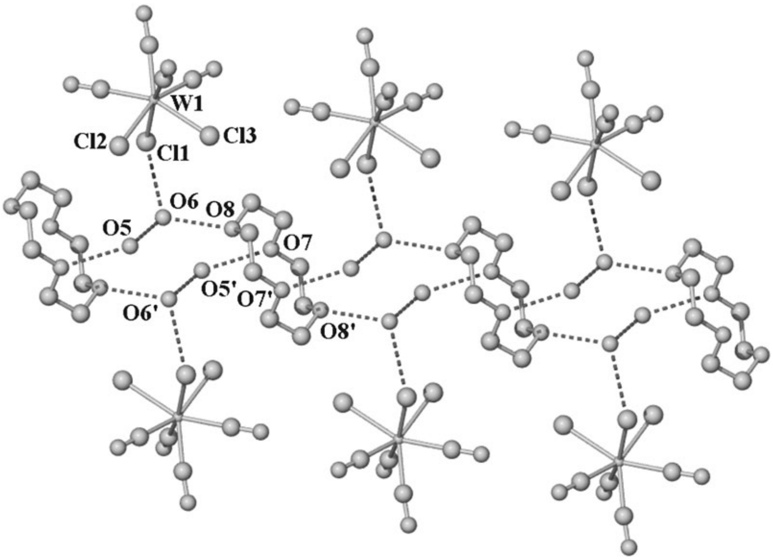

Fig. 22 X-Ray crystal structure of the polymeric chain in $[(H_5O_2^+)_2 \cdot 12C4][W(CO)_4Cl_3]_2$.[62]

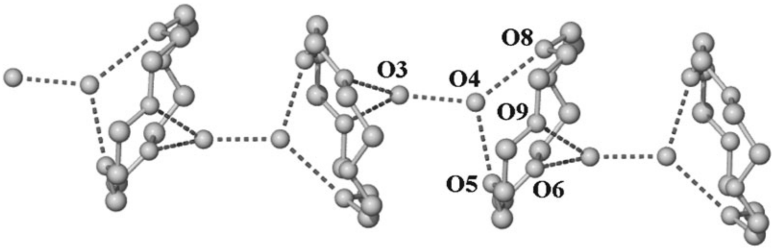

Fig. 23 X-Ray crystal structure of the $[H_5O_2^+ \cdot 15C5]_n$ polymeric chain in $[H_5O_2^+ \cdot 15C5][MOCl_4(H_2O)]$, (M = Mo, W).[70]

of this ion is presumably significantly higher than the lowest energy structures considered, *viz*. bent/pyramidal symmetric/asymmetric structures.

The $H_5O_2^+$ oxonium ion in $[(H_5O_2^+)_2 \cdot 12C4][W(CO)_4Cl_3]_2$ has an O···O separation of 2.387(8) Å.[62] The crown ether/oxonium ion part of the structure involves 12C4 molecules spanning two $H_5O_2^+$ ions in a polymeric strand (Fig. 22). The $H_5O_2^+$ ions are involved with hydrogen bonding interactions with the $[W(CO)_4Cl_3]^-$ anions but are more than 3.5 Å from adjacent $H_5O_2^+$ ions excluding the possibility of any further oxonium ion/oxonium ion interactions.

For molybdenum or tungsten chemistry involving 15C5 macrocycles there is not a size match between the metal and crown ether, so the macrocycle is not suitable for metal ion complexation, and $[MOCl_4(H_2O)]^-$ anions, which are typically observed in these types of reactions with aqueous acid, are isolated (*e.g*. in refs. 39, 43 and 45). Accordingly, $[H_5O_2^+ \cdot 15C5][MOCl_4(H_2O)]$ (M = Mo, W) complexes were identified. The $H_5O_2^+$ oxonium ion in both of these complexes successively bridge 15C5 molecules to form polymeric hydrogen bonded strands (Fig. 23).[71] It is encouraging that in both complexes, the $H_5O_2^+$ ion was isolated, and further studies may show the selectivity of 15C5 for $H_5O_2^+$ in these structures, but it must be kept in mind there many other factors in this chemistry to be considered such as intermolecular hydrogen bonding and crystal packing forces that can determine the

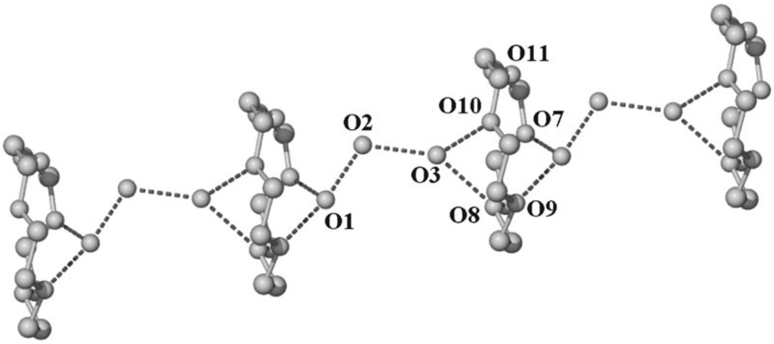

Fig. 24 X-Ray crystal structure of the $[H_7O_3^+ \cdot 15C5]_n$ polymeric chain in $[H_7O_3^+ \cdot 15C5][AuCl_4]$.[69,73]

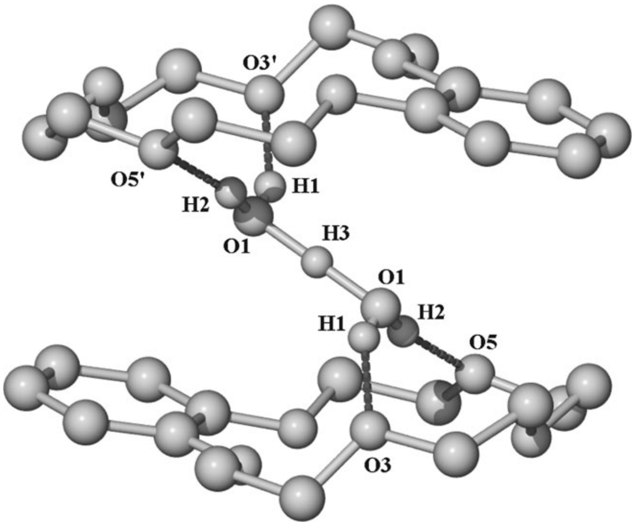

Fig. 25 X-Ray crystal structure of the [$H_5O_2^+$·(benzo-15C5)] sandwich cation in [$H_5O_2^+$·(benzo-15C5)][$AuCl_4$].[73]

type of oxonium ion isolated. The $H_5O_2^+$ oxonium ions here have the lowest energy staggered conformation,[73] and have slightly shorter O···O distances (2.399(2) and 2.383(2) Å) than typically encountered (2.41–2.45 Å)[2,13] and may be due to the compression of the ion between the two 15C5 molecules. As for most [H_3O^+·18C6] complexes, the only hydrogen bonding contacts are between the crown ether and the oxonium ions. However, in contrast to [H_3O^+·18C6] ions, where the cations are generally isolated as discrete entities, the [$H_5O_2^+$·15C5] ions form polymeric strands similar to several oxonium ion/12C4 complexes (see above). With this in mind, it may be possible to crystal engineer a large range of arrays by judicious choice of hydrogen bond donors and acceptors of these types.

In [$H_7O_3^+$][$AuCl_4$]·15C5, an $H_7O_3^+$ oxonium ion spans successive 15C5 molecules in a one-dimensional hydrogen bonded array (Fig. 24). This compound was formed by reaction of an *aqua regia* solution of gold with 15C5.[70,74] The $H_7O_3^+$ ion is unsymmetrical with O···O distances of 2.43(2) and 2.536(18) Å and is remarkably close to being described as an $H_5O_2^+$ ion hydrogen bonded to a water molecule. The O···O···O angle is 121°. If benzo-15C5 is used in place of 15C5 in the above reaction, [$H_5O_2^+$][$AuCl_4$]·(benzo-15C5) is formed. Here, a sandwich complex is observed where the *trans* $H_5O_2^+$ ion is hydrogen bonded between two crown ethers as a discrete cationic unit and it is intriguing that a small change in the rigidity of the crown ether (by incorporation of the benzo substituent) can bring about such a drastic structural change (Fig. 25).[74] A similar structure has been found in [(benzo-15C5)$_2$·$H_5O_2^+$][(benzo-15C5)$_2$·H_3O^+][TaF_6]$_2$ which also has the unusual situation where H_3O^+ is sandwiched between two 15C5 molecules.[49]

3. Conclusions

Crown ethers can be used to isolate oxonium ions $H^+·(H_2O)_n$ (n = 1, 2, 3, 4). The structural nature and oligonuclearity of the oxonium ion depends on the hydrogen bonding acceptor properties of the immediate environment. In the medium of the experiments performed in this review, there are a plethora of hydrogen bonding acceptors, including crown ethers, heteroatoms as ligands on anionic residues and halide ions. 18C6 reliably binds the H_3O^+ oxonium ion almost selectively, while 21C7 and dicyclohexano-24C8 and dibenzo-24C8 traps $H_5O_2^+$ ions and 30C10 binds two H_3O^+ ions (although there are only limited examples of the latter two). Intriguing species were isolated when smaller crown ethers than 18C6, *viz*. 12C4 and 15C5 were used, which crystallise with larger aggregate oxonium ions $H^+·(H_2O)_n$ (n = 2, 3, 4) as linkers between successive crown ethers and crystallise as polymeric strands. The smaller macrocycles are not large enough to totally encapsulate the H_3O^+ ion and rather bind as hydrogen bond acceptors between alternating oxonium ions and crown ethers.

References

1 P. Walden, *Salts, Acids and Bases: Electrolytes: Stereochemistry*, McGraw-Hill, New York, 1929, p. 60.
2 C. I. Ratcliffe and D. E. Irish, *The Nature of the Hydrated Proton, Part One: The Solid and Gaseous States, in Water Science Reviews 3*, Cambridge University Press, Cambridge, UK, 1988, pp. 149–207.
3 E. N. da C. Andrade, *Rutherford and the Nature of the Atom*, Doubleday, New York, 1964, p. 164.
4 J. N. Brønsted, *Recl. Trav. Chim. Pays-Bas*, 1923, **42**, 718.
5 T. M. Lowry, *Chem. Ind. (London)*, 1923, **42**, 43.
6 M. Volmer, *Justus Liebigs Ann. Chem.*, 1924, **440**, 200.
7 R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261.
8 Y. Kakiuchi, H. Shono, H. Komatsu and K. Kigoshi, *J. Chem. Phys.*, 1951, **19**, 1069.
9 E. Wicke, M. Eigen and Th. Ackermann, *Z. Phys. Chem., Neue Folge*, 1954, **1**, 340.
10 M. Eigen and L. De Maeyer, in *The Structure of Electrolytic Solution*, ed. W. J. Hamer, Wiley, New York, 1959, ch. 5, p. 64.
11 N. W. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 738.
12 E. S. Stoyanov, K.-C. Kim and C. A. Reed, *J. Am. Chem. Soc.*, 2006, **128**, 1948.
13 H.-S. Andrei, S. A. Nizkorodov and O. Dopfer, *Angew. Chem., Int. Ed.*, 2007, **46**, 4754.
14 O. Coskuner, E. A. A. Jarvis and T. C. Allison, *Angew. Chem., Int. Ed.*, 2007, **46**, 7853.
15 A. Potier, J. M. Leclercq and M. Allavena, *J. Phys. Chem.*, 1984, **88**, 1125.
16 D. Steinborn, O. Gravenhorst, H. Hartung and U. Baumeister, *Inorg. Chem.*, 1997, **36**, 2195.
17 H. Henke and W. H. Kuks, *Z. Kristallogr.*, 1987, **181**, 113.
18 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 2495.
19 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
20 G. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, Cambridge, 1991.
21 J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351.
22 J. S. Bradshaw and R. M. Izatt, *Acc. Chem. Res.*, 1997, **30**, 338.
23 R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem. Rev.*, 1991, **91**, 1721.
24 J. J. Christensen, J. O. Hill and R. M. Izatt, *Science*, 1971, **174**, 459.
25 D.J. Cram., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1039.
26 R. D. Hancock, *J. Chem. Educ.*, 1992, **69**, 615.
27 *Advanced Inorganic Chemistry*, Wiley-Interscience, ed. F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, New York, 6th edn, 1999, p. 55.
28 For example, N. P. Rath and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1985, 665.
29 J.-P. Behr, P. Dumas and D. Moras, *J. Am. Chem. Soc.*, 1982, **104**, 4540.
30 P. D. J. Grootenhuis, J. W. H. M. Uiterwijk, D. N. Reinhoudt, C. J. van Staveren, E. J. R. Sudholter, M. Bos, J. van Eerden,

W. T. Klooster, L. Kruise and S. Harkema, *J. Am. Chem. Soc.*, 1986, **108**, 780.

31 C. B. Shoemaker, L. V. McAfree, D. P. Shoemaker and C. W. Dekock, *Acta Crystallogr., Sect. C*, 1986, **42**, 1310.

32 J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone and C. M. Means, *J. Am. Chem. Soc.*, 1987, **109**, 8100.

33 W. Ming, W. Boyi, Z. Peiju, W. Wenji and L. Jie, *Acta Crystallogr., Sect. C*, 1988, **44**, 1913.

34 R. Chenervert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1989, **67**, 32.

35 R. Chenervert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1990, **68**, 797.

36 J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang and M. T. May, *Inorg. Chem.*, 1990, **29**, 467.

37 J. L. Atwood, S. G. Bott, K. D. Robinson, E. J. Bishop and M. T. May, *J. Crystallogr. Spectrosc. Res.*, 1991, **21**, 459.

38 R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins and R. F. Henry, *Inorg. Chem.*, 1991, **30**, 2671.

39 V. S. Sergienko, L. Kh. Minacheva, N. Kh. Ashurova, M. A. Porai-Koshits, K. G. Yakubov and V. G. Sakharova, *Russ. J. Inorg. Chem.*, 1991, **36**, 381.

40 P. C. Junk and J. L. Atwood, *J. Chem. Crystallogr.*, 1994, **24**, 247.

41 J. L. Atwood, P. C. Junk, M. T. May and K. D. Robinson, *J. Chem. Crystallogr.*, 1994, **24**, 243.

42 P. C. Junk, L. R. MacGillivray, M. T. May, K. D. Robinson and J. L. Atwood, *Inorg. Chem.*, 1995, **34**, 5395.

43 J. L. Atwood, P. C. Junk, M. T. May and K. D. Robinson, *J. Coord. Chem.*, 1996, **40**, 247.

44 J. L. Atwood, S. G. Bott, P. C. Junk and M. T. May, *J. Organomet. Chem.*, 1995, **487**, 7.

45 J. L. Atwood, S. G. Bott, P. C. Junk and M. T. May, *J. Coord. Chem.*, 1996, **37**, 89.

46 A. Alvanipour, J. L. Atwood, S. G. Bott, P. C. Junk, U. H. Kynast and H. Prinz, *J. Chem. Soc., Dalton Trans.*, 1998 1223.

47 L. J. Barbour, L. R. MacGillivray and J. L. Atwood, *J. Chem. Crystallogr.*, 1996, **26**, 59.

48 M. Calleja, K. Johnson, W. J. Belcher and J. W. Steed, *Inorg. Chem.*, 2001, **40**, 4978.

49 M. S. Fonari, Y. A. Simonov, W.-J. Wang, S.-W. Tang, E. V. Ganin, V. O. Gelmboldt, T. S. Chernaya, O. A. Alekseeva and N. G. Furmanova, *Polyhedron*, 2007, **26**, 5193.

50 H. Hassaballa, J. W. Steed, P. C. Junk and M. R. J. Elsegood, *Inorg. Chem.*, 1998, **37**, 4666.

51 J. L. Atwood, in *Inclusion Compounds*, ed. J. L. Atwood, J. D. Davies and D. D. MacNicol, Academic Press, London, 1984, vol. 4, pp. 375–405.

52 J. L. Atwood, in *Chemical Separations*, ed. C. J. King and J. D. Navratil, Litarvan, Denver, 1986, pp. 335–354.

53 J. L. Atwood, in *Separation Technology*, ed. N. N. Li and H. Strathmann, United Engineering Trustees, New York, 1988, pp. 46–56.

54 P. C. Junk and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 1995, 1551.

55 P. C. Junk and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, 1997, 4393.

56 R. D. Rogers and M. M. Benning, *J. Inclusion Phenom., Mol. Recogn.*, 1991, **11**, 121.

57 M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 345.

58 J. Hasek, D. Hlavata and K. Huml, *Acta Crystallogr., Sect. B*, 1980, **36**, 1782.

59 N. K. Dalley, R. M. Izatt and J. J. Christensen, *Synthetic Multidentate Macrocyclic Compounds*, Academic Press, New York, 1978, pp. 207–44.

60 E. M. Holt, N. W. Alcock, R. R. Hendrixson, G. D. Malpass, Jr, R. G. Ghirardelli and R. A. Palmer, *Acta Crystallogr., Sect. B*, 1981, **37**, 1080.

61 M. L. Cole, C. Jones and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 2002, 896.

62 H. Hassaballa, J. W. Steed and P. C. Junk, *Chem. Commun.*, 1998, 577.

63 J. L. Atwood and P. C. Junk, *J. Coord. Chem.*, 2000, **51**, 379.

64 H. Feinberg, I. Columbus, S. Cohen, M. Rabinovitz, H. Selig and G. Shoham, *Polyhedron*, 1993, **12**, 1811.

65 A. Bino and F. A. Cotton, *J. Am. Chem. Soc.*, 1979, **101**, 4150.

66 B. Chiswell, E. D. McKenzie and L. F. Lindoy, in *Comprehensive Coordination Chemistry*, ed. G, Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, New York, 1987, vol. 4, p. 80.

67 J. L. Atwood and P. C. Junk, *Polyhedron*, 2000, **19**, 85.

68 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

69 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

70 M. Calleja, S. A. Mason, P. D. Prince, J. W. Steed and C. Wilkinson, *New J. Chem.*, 2001, **25**, 1475.

71 P. C. Junk and J. L. Atwood, *J. Organomet. Chem.*, 1998, **565**, 179.

72 A. Bino and F. A. Cotton, *J. Am. Chem. Soc.*, 1980, **102**, 608.

73 Y. I. Yeh, M. Okamura, J. D. Myers, J. M. Price and Y. T. Lee, *J. Chem. Phys.*, 1989, **91**, 7319.

74 J. W. Steed and K. Johnson, *Chem. Commun.*, 1998, 1479.