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Stabilisation of sodium complexes of 18-crown-6 by intramolecular hydrogen bonding†

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Complexation of Na^+ by 18-crown-6 within an aqueous medium resulted in the formation of the monohydrates [Na(18-crown-6)(H_2O)(X)] (X = ClO_4, NO_3 or ReO_4) in the presence of oxygen donor anions. All three complexes exhibit a significant intramolecular hydrogen bond between the co-ordinated water molecule and the crown ether as well as structure organising C–H···O interactions. In the presence of anions with less affinity for Na^+, complexes of type [Na(18-crown-6)$(H_2O)_2$]X (X = N_3 or I_3) were formed. In the case of the azide both water molecules hydrogen bond strongly with the crown ligand giving rise to a highly unsymmetrical complex. In the triiodide more symmetrical intramolecular interactions are observed, as well as intermolecular water–crown hydrogen bonds. Reaction of $NaBPh_4$ with 18-crown-6 in aqueous ethanol resulted in the formation of [Na_2(18-crown-6)$_2$$(H_2O)_3$][$BPh_4$]$_2$ in which strong intramolecular hydrogen bonds are observed for both bridging and terminal water ligands in a similar fashion to the azide **4a**. The bridging aqua ligands interact with both crown ether hydrogen bond acceptors.

Introduction

The early, and appealing, postulate that the selectivity of macrocyclic hosts such as the crown ethers for alkali metal cation guests depends largely upon the size match between ionic diameter and macrocycle cavity size has undergone a great deal of revision and elaboration since the discovery of these hosts in 1967.[1] In particular, properties such as degree of preorganisation and the rigidity of the macrocycle have been shown to be crucial by wide ranging systematic studies. Factors such as cation charge, solvent and solvation free energy, chelate ring size and the number and type of donor groups are also highly important in determining host selectivity.[2–6] The interplay of all of these considerations makes the isolation and study of particular aspects of cation co-ordination difficult since the system must be viewed as a synergistic whole, particularly in the case of highly flexible molecules such as the crown ethers and related corands. We have recently begun a research programme aimed at the examination of the influence of non-covalent interactions, especially hydrogen bonds, on the structures and complexation behaviour of supramolecular systems.[7–12] Such systems, notably those involving very weak interactions of the C–H···X type[13–15] or with crystal engineering potential, are highly topical.[16–24] In particular, we have found that systems which are either sterically or electronically mismatched have proved interesting by virtue of the distorted structures adopted in order to maximise the number of weak interactions stabilising the system as a whole. For example, the mismatched hydrogen bonded chain [$UO_2Cl_2(H_2O)_3$]$_{16}$(15-crown-5)$_{16}$ exhibits *sixteen* unique metal complexes and crown ethers before the pattern is able to repeat itself, as a consequence of the directionality of the multiple hydrogen bonds holding the complex together.[7] In terms of electronically mismatched systems we have examined the binding of the soft metal ion Ag^+ with the relatively hard ligand 15-crown-5 and substituted derivatives.[8] In these cases, the degree of crown flexibility results in two packing modes characterised by the presence or absence of significant C–H···O intermolecular hydrogen bonds. In view of the manifest selectivity of 18-crown-6 for K^+ over all of the other alkali metals [log K_a (MeOH, 25 °C) 6.10, *cf.* 4.32, 5.35 and 4.62 for Na^+, Rb^+ and Cs^+ respectively[2]] we have chosen to investigate the structures of complexes of the non-complementary pair Na^+/18-crown-6 prepared from a variety of solvents and in the presence of both hard and soft anions.

Results and discussion

Examination of the Cambridge Crystallographic database reveals a total of 52 structures containing Na^+ complexes of 18-crown-6 or its derivatives, frequently acting as a counter ion to more "interesting" anions.[25] Surprisingly, in the vast majority of cases, Na^+ actually exhibits a good fit within the 18-crown-6 ring. In general, in relatively non-polar media such as tetrahydrofuran (thf), Na^+ forms complexes of type [Na(18-crown-6)(thf)$_2$]$^+$ **1** in which the Na^+ ion exhibits approximately equal equatorial bond distances to all six crown oxygen atoms of 2.76–2.80 Å, while thf molecules occupy axial co-ordination sites above and below the crown ether. The O_{thf}–Na–O_{thf} vector is essentially normal to the plane containing the six crown oxygen atoms, and exhibits a bond angle of 180°. The fact that 18-crown-6 is too large to bind Na^+ is only evidenced by the rather long Na–O distances.[26,27] In contrast, we find that in aqueous media, in the presence of O-donor anions, complexes of type [Na(18-crown-6)(H_2O)(X)] (X = ClO_4 **2a**; NO_3 **2b**; or ReO_4 **2c**) are formed in which the anion is co-ordinated to the hard, oxophilic Na^+ cation. The crystal structure of the perchlorate complex **2a** (Fig. 1; crystallographic data for all new complexes are summarised in Table 3) demonstrates a significantly distorted O_3ClO–Na–OH_2 bond angle of 163.18(8)° and, in contrast to **1**, the Na^+ cation is situated significantly to one side of the macrocyclic cavity with Na–O_{crown} distances ranging from 2.5871(17) to 3.1770(18) Å, Table 1. This highly unsymmetrical co-ordination is apparently a direct result of the presence of an *intramolecular* hydrogen bonding interaction between the co-ordinated water molecule and one of the crown oxygen atoms,

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† 18-crown-6 = 1,4,7,10,13,16-Hexaoxacyclooctadecane.

Table 1 Selected distances (Å) for Na$^+$ complexes of 18-crown-6

Complex 2a			
Na(1)–O(1)	2.345(2)	Na(1)–O(3a)	2.6316(15)
Na(1)–O(2)	2.385(2)	Na(1)–O(4a)	2.8132(16)
Na(1)–O(1a)	2.6014(16)	Na(1)–O(5a)	3.1770(18)
Na(1)–O(2a)	2.5871(17)	Na(1)–O(6a)	2.9008(16)
Complex **2b**			
Na(1)–O(1)	2.4782(12)	Na(1)–O(3a)	2.4688(10)
Na(1)–O(2)	2.5634(11)	Na(1)–O(4a)	2.5828(10)
Na(1)–O(4)	2.3402(11)	Na(1)–O(5a)	3.2380(12)
Na(1)–O(1a)	2.6130(10)	Na(1)–O(6a)	3.6460(12)
Na(1)–O(2a)	2.5792(11)		
Complex **2c**			
Na(1)–O(1)	2.365(7)	Na(1)–O(3a)	2.643(6)
Na(1)–O(2)	2.310(7)	Na(1)–O(4a)	2.732(6)
Na(1)–O(1a)	2.698(8)	Na(1)–O(5a)	2.970(6)
Na(1)–O(2a)	2.650(7)	Na(1)–O(6a)	2.917(6)
Complex **4a**			
Na(1)–O(11)	2.296(4)	Na(1)–O(3a)	2.822(2)
Na(1)–O(1)	2.304(4)	Na(1)–O(1a)[1]	3.225(2)
Na(1)–O(1a)	2.430(2)	Na(1)–O(2a)[1]	3.191(2)
Na(1)–O2(a)	2.443(2)	Na(1)–O(3a)[1]	2.757(2)
Complex **4b**			
Na(1)–O(1)	2.322(2)	Na(1)–O(3a)	2.765(2)
Na(1)–O(1a)	2.753(2)	Na(1)–O(2a)	2.792(2)
Complex **5**			
Na(1)–O(2)[1]	2.307(14)	Na(1)–O(3a)	2.394(4)
Na(1)–O(2)	2.383(15)	Na(1)–O(4a)	2.523(4)
Na(1)–O(1)	2.389(5)	Na(1)–O(5a)	2.696(4)
Na(1)–O(2a)	2.851(4)		

Symmetry operator used to generate equivalent atoms: 1 $-x + 1$, $-y + 2$, $-z + 1$.

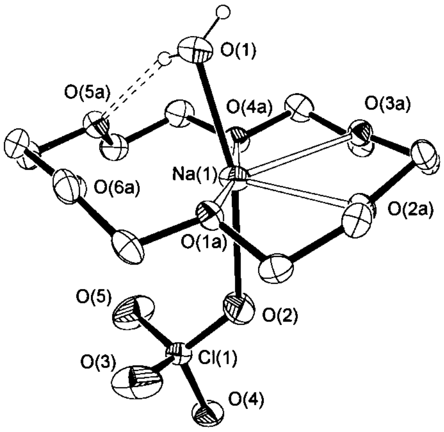

Fig. 1 Structure of [Na(18-crown-6)(H$_2$O)(ClO$_4$)] **2a**, exhibiting an intramolecular hydrogen bond.

Table 2 Selected hydrogen bond parameters (distances in Å, angles in °) for Na$^+$ complexes of 18-crown-6

D–H$\cdots$A	*d*(D–H)	*d*(H$\cdots$A)	*d*(D$\cdots$A)	DHA
Complex **2a**				
O(1)–H(2)$\cdots$O(5a)[a]	0.80(5)	2.16(5)	2.919(3)	157(4)
O(1)–H(1)$\cdots$O(4)[1]	0.84(5)	2.26(5)	3.098(3)	176(4)
Complex **2b**				
O(4)–H(42)$\cdots$O(6a)[a]	0.79(3)	2.36(3)	3.1061(16)	157(2)
O(4)–H(41)$\cdots$O(3)[2]	0.89(2)	1.95(2)	2.8275(15)	170.1(18)
Complex **2a**[a]				
O(1)$\cdots$O(5a)[a]			3.136(6)	
O(1)$\cdots$O(5)			2.816(7)	
Complex **4a**[b]				
O(1)$\cdots$O(1a)[a]			2.876(4)	
O(11)$\cdots$O(2a)[a]			2.889(4)	
O(1)$\cdots$N(3s)			2.830(4)	
O(11)$\cdots$N(3s)			2.866(4)	
Complex **4b**				
O(1)–H(12)$\cdots$O(2a)[3]	0.77(7)	2.25(6)	2.842(3)	135(6)
O(1)–H(11)$\cdots$O(3a)[4]	0.73(5)	2.31(5)	3.005(3)	157(5)
Complex **5**[b]				
O(1)$\cdots$O(1a)[a]			2.696(5)	
O(2)$\cdots$O(4a)[a]			2.741(18)	

Symmetry transformations used to generate equivalent atoms: 1 $x - \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; 2 $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$; 3 $-x + 1$, $-y + 2$, $-z + 1$; 4 $-x + 1$, y, $-z + \frac{3}{2}$. [a] Intramolecular hydrogen bond. [b] Hydrogen atoms not located.

O(1)$\cdots$O(5a) 2.919(3) Å; Fig. 1, Table 2. While this distance is at the longer end of the range normally observed for O–H$\cdots$O hydrogen bonds it must be remembered that this interaction forms part of a strained, non-covalent chelating system. The water molecule must balance its affinity for both the crown oxygen atom and the sodium cation, while the whole system is limited by the flexibility of the crown ether. Clear evidence for the hydrogen bonded interaction comes from the positions of the water hydrogen atoms which were located experimentally, with H(2) directed towards the crown oxygen atom; H(2)$\cdots$O(5a) 2.16(5) Å, O–H$\cdots$O angle of 157(4)°. Indeed, in charged systems the basis of the strength–length analogy has recently been called into question.[17] The remaining hydrogen atom of the water molecule is hydrogen bonded to the perchlorate anion of an adjacent complex, to give an infinite hydrogen bonded chain. The complex is further stabilised by intramolecular C–H$\cdots$O interactions[15] between a non-co-ordinated oxygen atom of the perchlorate anion and the relatively acidic crown ethylenic backbone, with C(8a)$\cdots$O(5) 3.330(2) Å and a C–H$\cdots$O angle of 147° (C–H distance normalised to 0.99 Å).

The involvement of a water molecule in an intramolecular hydrogen bonding interaction is also present in a similar way in complexes **2b** and **2c** and clearly results in a significant stabilisation of the "[Na(18-crown-6)(H$_2$O)]$^+$" unit. In the case of complex **2b** the Na$^+$ cation is again forced to one side of the macrocyclic cavity in contrast to complexes such as **1** (Table 1), allowing the co-ordinated water molecule to approach a crown oxygen atom, O(4)$\cdots$O(6a) 3.1061(16) Å, Fig. 2. Also, as with **2a**, the remaining water hydrogen atom interacts with an adjacent nitrate oxygen atom, O(4)$\cdots$O(3) 2.8275(15) Å. The nitrate anion is also able to form a further intramolecular C–H$\cdots$O interaction, O(1)$\cdots$C(11) 3.309(2) Å, H(11a)$\cdots$O(1) 2.36 Å. Complex **2b** differs from **2a** however in that the nitrate anion adopts a chelating co-ordination mode with Na–O distances of 2.4782(12) and 2.5634(11) Å, compared to a single short Na–OClO$_3$ distance of 2.385(2) Å. This results in a greater steric demand on the face of the crown ether adjacent to the nitrate anion. This is apparently sufficient to result in a change in behaviour such that, in contrast to **2a**, the intramolecular hydrogen bond to water now becomes much longer (and perhaps weaker) than the intermolecular interaction. Also, despite the similarity of the hydrogen bonded geometries, the crown conformation in **2b** is entirely different to that in **2a**. In **2a** the crown ether adopts a relatively flat conformation, similar to that observed in **1**. In contrast the non-co-ordinated crown oxygen atoms O(5a) and O(6a) in compound **2b** are significantly out of the plane of the remaining four. At first sight this is apparently in order to maximise the intramolecular hydrogen bonding to the co-ordinated water molecule. The fact that the

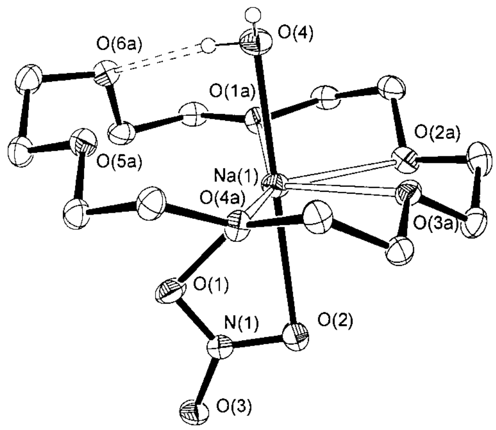

Fig. 2 Structure of [Na(18-crown-6)(H_2O)(NO_3)] **2b**, exhibiting an intramolecular hydrogen bond.

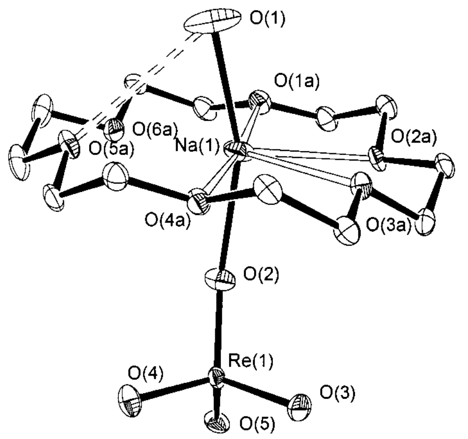

Fig. 3 Structure of [Na(18-crown-6)(H_2O)(ReO_4)] **2c**, exhibiting an intramolecular hydrogen bond.

O–H · · · O distance is longer in **2b** however points to a different explanation. It is possible that the crown conformation is actually governed by the short C–H · · · O interaction detailed above. By distorting in **2b**, the crown is able to orientate a methylene group towards an oxygen atom of the co-ordinated nitrato ligand. Conversely, in compound **2a** the perchlorate anion which acts as an acceptor of this 'weak' interaction is not chelating and is thus both further from the metal centre, and more conformationally mobile, hence much less crown distortion is required.

In complex **2c** the large ReO_4^- anion makes a very close approach to the Na^+ cation, with Na–O(2) 2.310(7) Å, however the longer Re–O distances compared to the Cl–O bonds in **2a** preclude the close approach of the crown ethylene backbone to the co-ordinated anion, and indeed the two materials are not isostructural, Fig. 3. The hydrogen bonding to water however is still present in the same way as for **2a** and **2b**. As for **2b** the longer $O_{water} \cdots O_{crown}$ distances (Table 2) point to the dominance of intermolecular hydrogen bonding over intramolecular effects, although the highly non-linear O(1)–Na–O(2) vector of 158.5(4)° still indicates the presence of a significant intramolecular interaction.

These results contrast significantly to the known structure of [Na(18-crown-6)(H_2O)][SCN] **3** in which the SCN^- anion is not co-ordinated to the Na^+ centre and the crown is significantly distorted in order to occupy the resulting vacant axial site with an etheric oxygen atom. The resulting conformation does not admit intramolecular hydrogen bonding and instead the apical water is hydrogen bonded solely to the N atoms of a pair of anions, which bridge between pairs of cations.[28] Both intramolecular and intermolecular hydrogen bonding is observed, however, for the europium 15-crown-5 complex [Eu(15-crown-5)(H_2O)$_2$(NO_3)$_3$]·15-crown-5 in which the large Eu^{3+} ion adopts a perching co-ordination mode which is much less geometrically restricting and binds to only two crown oxygen atoms. One europium-co-ordinated water molecule hydrogen bonds to two adjacent crown oxygen atoms with O · · · O distances of 2.751 and 2.804 Å.[29] In contrast to these hydrated species, in the KNO_3 complex of 18-crown-6, the nitrato anion chelates one face of the K^+ ion, which is situated slightly above the plane of the crown ether. No water is included in the structure.[30]

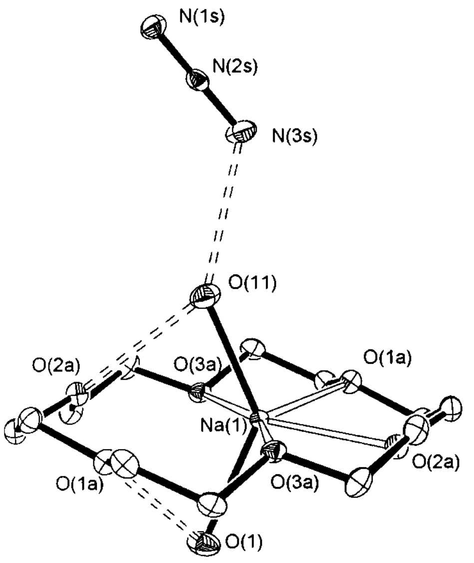

Fig. 4 Structure of [Na(18-crown-6)(H_2O)$_2$][N_3] **4a** showing two intramolecular hydrogen bonds.

Clearly, the anions, X, are also involved in the co-ordination of the Na^+ ion in complexes **2** and hence the structures of the 18-crown-6 complexes of relatively non-co-ordinating anions N_3^- and I_3^- were examined in anticipation of comparison with **3**. However, the resulting species, [Na(18-crown-6)(H_2O)$_2$]X (X = N_3 **4a** or I_3 **4b**), exhibit two axially co-ordinated aqua ligands. In the case of **4a** both water molecules take part in intramolecular hydrogen bonds of the type observed in complexes of type **2**, with $O_{water} \cdots O_{crown}$ 2.882(5) Å and an extremely low O_{water}–Na–O_{water} angle of 131.4(2)° (averages over two crystallographically independent molecules), Fig. 4. The sodium cation is forced far over onto one side of the crown in order to accommodate the pair of intramolecular hydrogen bonded interactions (Table 2) while the azide anion bridges *via* hydrogen bonding from one Na(H_2O)$_2^+$ unit to the next. Clearly the presence of two water molecules, coupled with the lower electronegativity of the N-acceptor anion, results in a significant increase in the importance of the intramolecular hydrogen bonding stabilisation. In the case of the analogous I_3^- complex **4b** the low electronegativity of the iodine atoms in the anion results in no water–anion interaction whatsoever. Instead, the aqua ligands hydrogen bond to crown ether oxygen atoms both intramolecularly and intermolecularly, $O_w \cdots O_{crown}$ 2.842(3) and 3.005(3) Å, $H \cdots O_{crown}$ refined to 2.25(6) and 2.31(5) Å, respectively. This results in a linear O–Na–O vector which contrasts significantly with that in **4a** and a much more symmetrical co-ordination of the Na^+ ion within the crown, with slightly shorter distances to O(1a) and O(3a), 2.759(2) Å, than O(2a) [2.792(2) Å] which takes part in the intramolecular hydrogen bond. Fascinatingly, however, the O_w–Na–O_w vector is not normal to the crown ether plane, as in the case of **1**, but intersects it an angle of 77.0° in order to maximise $H_2O \cdots O_{crown}$ hydrogen bonds, Fig. 5. A similar hydrogen bonded geometry has been observed for the Na(H_2O)$_2^+$ complex of 2,3,11,12-tetraphenyl-18-crown-6. This was suggested to arise from steric interactions with the phenyl groups. Its observation in **4b** argues against this explanation.[31]

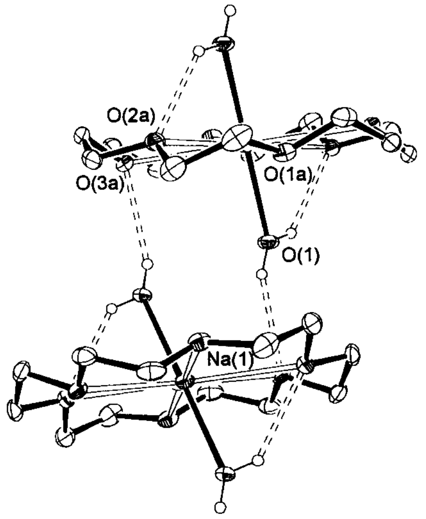

Fig. 5 Structure of [Na(18-crown-6)$(H_2O)_2$][I_3] **4b** showing intra- and inter-molecular hydrogen bonding.

These results contrast with the structure of [Na(*cis-anti-cis*-dicyclohexyl-18-crown-6)$(H_2O)_2$]Br in which the O_w-Na–O_w is linear and orthogonal to the crown ether plane, with no short intramolecular contacts.[32] The logarithm of the Na^+ binding constant for this macrocycle in methanol at 25 °C is 3.68, markedly lower than that of 18-crown-6 itself (log $K_a = 4.32$). This suggests that the intramolecular hydrogen bonding interactions reported herein may be a non-negligible factor in the magnitude of the solution binding constants of these ligands for Na^+. Clearly, however, the role of other well recognised factors, notably interactions with anions and orientation/preorganisation of the etheric dipoles, are also crucial since the analogous dibenzo-18-crown-6 complex with $Na(H_2O)_2^+$ in the presence of Br^- also does not exhibit intramolecular hydrogen bonds,[33] despite a log K_1 value of 4.36 (methanol, 25 °C, picrate salt).[2]

In view of the interesting results obtained for the non-co-ordinating anions N_3^- and I_3^- in complexes **4** we also examined the 18-crown-6 complex of $NaBPh_4$ in anticipation of confirming the geometry of the crown-co-ordinated $Na(H_2O)_2^+$ unit in the absence of significant interactions with the anions. Large, colourless crystals of composition Na·18-crown-6·$1.5H_2O$ were rapidly deposited from an ethanol–water solution (1 : 1 v/v). The crystal structure of this material proved fascinating although, reassuringly, consistent with the results described above. In fact the Na(crown) species was shown to be a binuclear dication containing one bridging and two terminal water molecules, Fig. 6, of overall formula [Na_2(18-crown-6)$_2(H_2O)_3$][BPh_4]$_2$·EtOH **5**. As with **4a** the complex is disordered over two orientations of the Na^+ and aqua ligands with the Na^+ cations occupying either one side of the relatively symmetrical macrocyclic cavity or the other. The entire complex resides upon a crystallographic inversion centre. In both orientations, both the bridging and terminal aqua ligands engage in the expected intramolecular hydrogen bonding interactions, with relatively short O···O contacts in the range 2.696(5)–2.808(4) Å (Table 2). The sodium ions and their associated ligands may be regarded as a close analogy of azide complex **4a**. In compound **4a** the bridging aqua ligand O(2) is hydrogen bonded to the N_3^- anion. In **5** it is also co-ordinated to the second cation, Na(1), as well as hydrogen bonding to the second macrocycle. Unfortunately, the crystallographic disorder makes a detailed comparison of bond angles difficult. This disorder apparently arises as a consequence of the ability to invert the entire $Na_2(H_2O)_3^{2+}$ unit within the symmetrical crown conformation, without materially affecting the steric volume occupied by the whole binuclear complex. A key comparison which must be made in these systems is that between compounds **5** and **4b**, both of which involve anions which do not significantly interact with the cationic complex. What is the reason for the formation of a bridged dimer in **5** and a mononuclear species in **4b**? It is possible that the answer to this question lies in the steric bulk of the anions. The I_3^- anion is small enough to pack in channels in between a hydrogen bonded polymeric array of $Na(H_2O)_2^+$–crown complexes. In contrast the BPh_4^- anions arrange themselves in pairs, effectively forming a vast cavity into which the Na_2(18-crown-6)$_2(H_2O)_3^{2+}$ cation fits. As a further complication to this remarkable complex there are two entirely independent pairs of "anion sandwiched" Na_2(18-crown-6)$_2(H_2O)_3^{2+}$ cations (both disordered as described above), which differ in their orientation with respect to the anion-pair cavities, Fig. 7. The Na(1) dicationic complex apparently interacts with the BPh_4^- aryl groups solely *via* hydrophobic inclusion of the edge of the crown between pairs of phenyl groups. There are also interactions from the terminal water ligands to highly disordered ethanol molecules. In con-

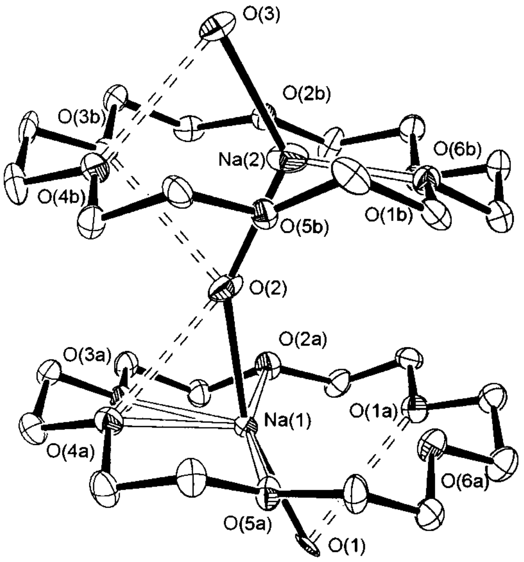

Fig. 6 Structure of the [Na_2(18-crown-6)$_2(H_2O)_3$]$^{2+}$ cation in complex **5**, exhibiting intramolecular hydrogen bonds.

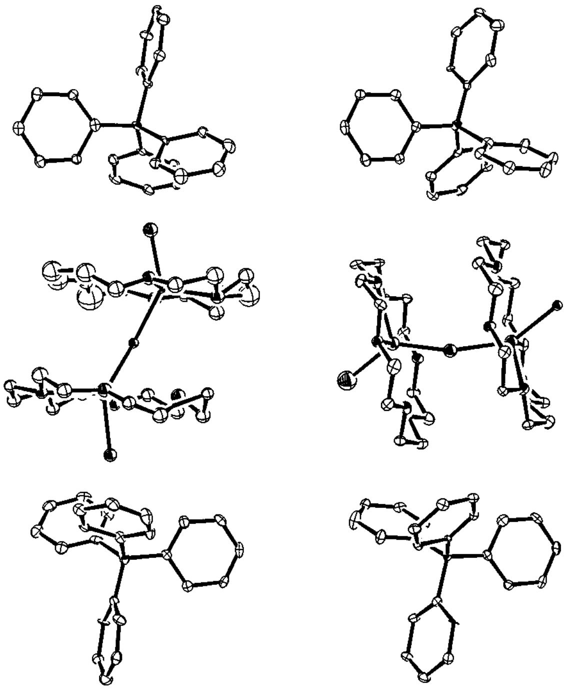

Fig. 7 Crystal packing in [Na_2(18-crown-6)$_2(H_2O)_3$][BPh_4]$_2$·EtOH **5** showing the orientations of the two independent complexes.

trast, the second dication engages in O–H · · · π hydrogen bonds with oxygen · · · centroid distances in the region of 3.3 Å with the second pair of anions. One possible explanation of this behaviour is that the incorporation of ethanol is necessary in order to hydrogen bond to the proton on the terminal aqua ligand, which is not intramolecularly hydrogen bonded to the crown. However, it appears that incorporation of *two* ethanol molecules would make the Na_2(18-crown-6)$_2$-$(H_2O)_3^{2+}$ · · · OHEt chain longer than the available space between the pair-wise $(BPh_4^-)_2$ cavities, causing inefficient crystal packing. As a result the second cation is forced to engage in a weak O–H · · · π interaction instead.

Conclusion

In terms of Na^+ co-ordination, these results represent an extreme example of the second of the four possible modes of co-ordination of metal ions, which are too small to fit within a macrocyclic cavity (unsymmetrical co-ordination), outlined by Dunitz *et al.*[34] They are of significance in the role of 18-crown-6 as a model for ionophore-mediated transport of Na^+ and K^+ ions across biological membranes, where the aqueous medium plays a significant role. The identification of this new kind of hydrogen bond in these complexes suggests a further contributing reason for decrease in selectivity of 18-crown-6 for K^+ over Na^+ in aqueous media, and gives insights into the high degree of solvent dependency of selectivity between different metal ions by ligands such as the crown ethers. Perhaps even more importantly, the structure of complex **5** illustrates the extraordinary lengths to which Nature is willing to go in order to ensure that the number of intermolecular interactions is at a maximum. As our understanding of weak interactions in the solid state grows the key question seems in every case to be not "is an atom interacting with anything?", but rather "what is it interacting with, and how may this interaction be maximised within the context of the rest of the structure?"

Experimental

Microanalyses were performed at University College London and at James Cook University. No precautions were taken to protect reaction mixtures from air or moisture and the majority of the products did not display significant moisture sensitivity when exposed to the atmosphere with the exception of complexes **2c** and **4a** which proved highly hygroscopic. Experimental conditions were designed to promote the formation of X-ray quality crystals and are unoptimised.

Preparations

[Na(18-crown-6)(H_2O)(ClO_4)] 2a. The salt $NaClO_4$ (0.047 g, 0.38 mmol), was dissolved in water (5 cm^3) and added to a solution of 18-crown-6 (0.1 g, 0.38 mmol) in water (5 cm^3). The product deposited as colourless blocks upon slow evaporation of the solution over a period of one week. Yield 0.089 g, 0.22 mmol, 58%. Calc. for $C_{12}H_{26}ClNaO_{11}$: C, 35.61; H, 6.47. Found: C, 35.5; H, 6.6%.

[Na(18-crown-6)(H_2O)(NO_3)] 2b. The salt $NaNO_3$ (0.032 g, 0.38 mmol) was dissolved in water (5 cm^3) and added to a solution of 18-crown-6 (0.1 g, 0.38 mmol) in methanol (5 cm^3). The product deposited as colourless blocks upon slow evaporation of the solution over a period of one week. Yield 0.088 g, 0.24 mmol, 62%. Calc. for $C_{12}H_{26}NNaO_{10}$: C, 39.24; H, 7.13; N, 3.81. Found: C, 39.3; H, 7.5; N, 3.7%.

[Na(18-crown-6)(H_2O)(ReO_4)] 2c. The salt $NaReO_4$ (0.10 g, 0.38 mmol) was dissolved in water (10 cm^3) and added to a solution of 18-crown-6 (0.1 g, 0.38 mmol) in methanol (10 cm^3). The product deposited as colourless blocks upon slow evaporation of the solution over a period of one week. Yield 0.072 g, 0.13 mmol, 35%. Attempts to obtain reliable elemental analysis were frustrated by the compound's extreme moisture sensitivity.

[Na(18-crown-6)(H_2O)][N_3] 4a. The salt NaN_3 (0.025 g, 0.38 mmol) was added to 18-crown-6 (0.1 g, 0.38 mmol) in a mixture of undried diethyl ether (5 cm^3) and dichloromethane (5 cm^3). The product deposited as colourless block over a period of twelve hours. Yield 0.09 g, 0.25 mmol, 65%. Attempts to obtain reliable elemental analysis were frustrated by the compound's extreme moisture sensitivity.

[Na(18-crown-6)(H_2O)][I_3] 4b. The salt NaI (0.057 g, 0.38 mmol) was dissolved in water (10 cm^3) and added to a solution of 18-crown-6 (0.1 g, 0.38 mmol) in water (10 cm^3). The product deposited long orange needles on slow evaporation of the solution over a period of six weeks. Yield: 0.027 g, 0.04 mmol, 10%. The I_3^- apparently arises as a consequence of the action of aerobic oxygen and light on the sample, which gradually turned from colourless to yellow during the course of the reaction. The limited availability of I_3^- accounts for both the low yield and long reaction time. Calc. for $C_{12}H_{28}I_3NaO_8$: C, 20.47; H, 4.01. Found: C, 22.0; H, 4.3%.

[Na_2(18-crown-6)$_2$(H_2O)$_3$][BPh_4]$_2$·EtOH 5. The salt $NaBPh_4$ (0.13 g, 0.38 mmol) was dissolved in ethanol (10 cm^3) and added to a solution of 18-crown-6 (0.1 g, 0.38 mmol) in water (10 cm^3). The product deposited as large colourless blocks on standing for twenty-four hours. Yield g, 0.15 mmol, 80%. The sample submitted for elemental analysis was powdered and allowed to stand in air for *ca.* one week resulting in loss of the ethanol solvent. Calc. for $C_{72}H_{70}B_2Na_2O_{15}$: C, 68.25; H, 7.48. Found: C, 68.3; H, 7.6%.

Crystallography

Crystal data and data collection parameters are summarized in Table 3. Crystals were mounted using a fast setting epoxy resin on the end of a glass fibre and cooled on the diffractometer to the temperature stated. All crystallographic measurements were carried out with a Nonius KappaCCD equipped with graphite monochromated Mo-Kα radiation using φ rotations with 2° frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN.[35] Data sets were corrected for Lorentz-polarisation effects and for the effects of absorption using the program Scalepack.[35] Structures were solved using the direct methods option of SHELXS 86[36] and developed using conventional alternating cycles of least squares refinement and Fourier-difference synthesis (SHELXL 97[37]) with the aid of the program X-Seed.[38] In general all non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. In the case of compounds **2a**, **2b** and **4b** water hydrogen atoms were located on the final Fourier-difference map and included within the model. It proved possible fully isotropically to refine them in these cases. Compounds **4a** and **5** proved to exhibit a significant disorder taking the form of two separate positions each of 50% occupancy for all of the sodium cations and co-ordinated water. In addition, two of the four independent crown ethers in **5** also proved to be disordered, although this was modelled effectively with each atom position showing clearly on Fourier-difference syntheses. All calculations were carried out either on a Silicon Graphics Indy R5000 workstation or an IBM-PC compatible personal computer.

CCDC reference number 186/1472.

See http://www.rsc.org/suppdata/dt/1999/2141/ for crystallographic files in .cif format.

Table 3 Crystallographic data for new complexes

	2a	**2b**	**2c**	**4a**	**4b**	**5**
Formula	$C_{12}H_{26}ClNaO_{11}$	$C_{12}H_{26}NNaO_{10}$	$C_{12}H_{27}NaO_{11}Re$	$C_{12}H_{26}N_3NaO_8$	$C_{12}H_{28}I_3NaO_8$	$C_{74}H_{93}B_2Na_2O_{15}$
Formula weight/g mol^{-1}	404.79	367.33	556.53	365.36	704.04	1290.08
T/°C	−100	−100	−150	−100	−150	−150
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$Pc2_1n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	9.1846(3)	12.0590(4)	7.9787(12)	9.5186(8)	20.6803(8)	13.4119(9)
b/Å	13.9712(5)	10.5053(3)	14.3770(6)	10.4064(9)	11.0480(5)	13.9456(10)
c/Å	14.6305(3)	14.0593(5)	16.9546(8)	11.0250(6)	10.8675(3)	22.5930(17)
α/°				67.825(2)		77.5320(2)
β/°		103.295(2)	98.254(2)	76.113(2)	109.989(2)	74.0820(2)
γ/°				67.551(2)		62.0940(2)
V/Å^3	1877.38(10)	1733.35(2)	1924.7(3)	928.8(3)	2333.38(15)	3572.1(4)
Z	4	4	4	2	4	2
μ/mm^{-1}	0.278	0.142	6.386	0.127	4.066	0.092
Reflections collected	16095	14177	16756	5761	10176	20041
Independent reflections	3448	3381	3648	3388	2241	11756
Parameters	227	226	227	245	121	1052
Goodness of fit of F^2	1.059	1.056	1.077	1.063	1.082	1.024
Final $R1$, $wR2$, $I > 2\sigma(I)$	0.0298, 0.0745	0.0325, 0.0788	0.0688, 0.1789	0.0606, 0.1611	0.0246, 0.0615	0.0617, 0.1366
(all data)	0.0319, 0.0766	0.0398, 0.0837	0.0716, 0.1831	0.0892, 0.1824	0.0266, 0.0628	0.0950, 0.1540
Largest difference peak/e Å^{-3}	0.22	0.17	4.33[a]	0.410	0.951	0.832

[a] Close to metal atom.

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References

1 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 2495.
2 F. de Jong and D. N. Reinhoudt, *Stability and Reactivity of Crown Ether Complexes*, Academic Press, London, 1981.
3 G. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, Cambridge, 1991.
4 R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem. Rev.*, 1991, **91**, 1721.
5 F. Vögtle, *Supramolecular Chemistry*, Wiley, New York, 1991.
6 J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle (Editors), *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, 1996, vol. 1.
7 J. W. Steed, H. Hassaballa and P. C. Junk, *Chem. Commun.*, 1998, 577.
8 P. D. Prince, J. W. Steed and P. J. Cragg, *Chem. Commun.*, 1999, in the press.
9 H. Hassaballa, J. W. Steed, P. C. Junk and M. R. J. Elsegood, *Inorg. Chem.*, 1998, 4666.
10 J. W. Steed, P. C. Junk and B. J. McCool, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3417.
11 J. W. Steed and K. Johnson, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2601.
12 J. W. Steed and K. Johnson, *J. Chem. Soc.*, *Chem. Commun.*, 1998, 1479.
13 M. Mascal, *Chem. Commun.*, 1998, 303.
14 R. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 566.
15 G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.
16 D. Braga, L. Maini and F. Grepioni, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2240.
17 D. Braga, F. Grepioni and J. J. Novoa, *Chem. Commun.*, 1998, 1959.
18 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.
19 B. M. Kariuki, K. D. M. Harris, D. Philp and J. M. A. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 12697.
20 N. N. L. Madhavi, A. K. Katz, H. L. Carrell, A. Nangia and G. R. Desiraju, *Chem. Commun.*, 1997, 1953.
21 N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63.
22 K. N. Rose, L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1998, 407.
23 K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595.
24 J. P. Campbell, J.-W. Hwang, V. G. Young, Jr., R. B. von Dreele, C. J. Cramer and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1998, **120**, 521.
25 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
26 D. J. Darensbourg, C. G. Bauch and A. L. Rheingold, *Inorg. Chem.*, 1987, **26**, 977.
27 S. I. Bailey, L. M. Englehart, W.-P. Leung, C. L. R. M. Ritchie and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1747.
28 M. Dobler, J. D. Dunitz and P. Seiler, *Acta Crystallogr.*, *Sect. B*, 1974, **30**, 2741.
29 M. Parvez, P. J. Breen and W. D. Horrocks, Jr., *Lanth. Actin. Res.*, 1988, **2**, 153.
30 J. W. Steed and P. C. Junk, unpublished work.
31 G. Weber, G. M. Sheldrick, T. Burgemeister, F. Dietl, A. Mannschreck and A. Merz, *Tetrahedron*, 1984, **40**, 855.
32 M. Mercer and M. R. Truter, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 2215.
33 M. A. Bush and M. R. Truter, *J. Chem. Soc. B*, 1971, 1440.
34 J. D. Dunitz, M. Dobler, P. Seiler and R. P. Phizackerley, *Acta Crystallogr.*, *Sect. B*, 1974, **30**, 2733.
35 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.
36 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A.*, 1990, **46**, 467.
37 G. M. Sheldrick, University of Göttingen, 1997.
38 L. J. Barbour, X-Seed, University of Missouri – Columbia, 1999.

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