The Crystal Structures of Three Alkali-metal Complexes with Cyclic Polyethers

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Summary The crystal structures are reported of sodium bromide with a 6-oxygen cyclic ether, sodium iodide with a 5-oxygen cyclic ether, and potassium iodide with a 10-oxygen ether; in the first two the cation is co-ordinated by additional entities but the 10-oxygen compound encloses the potassium completely.

Alkali-metal salts can be extracted into non-polar solvents by cyclic polyethers and form crystalline complexes with them.[1] The crystal structure of one of these complexes, $(\mathrm{Rb}_{0\cdot55}, \mathrm{Na}_{0\cdot45})\mathrm{NCS}(\text{dibenzo-18-crown-6})_{1\cdot5}$ has been determined.[2] Uncomplexed molecules of cyclic ether (systematically named 2,3:11,12-dibenzo-1,4,7,10,13,16-hexaoxocyclo-octadeca-2,11-diene) of crystallisation have a different conformation from those in the 1 : 1 metal complexes. The high proportion of sodium in the cation sites was surprising because the ligand extracts rubidium better than sodium,[3] and the Na–O distances were much larger than are normally found.[4] We have determined the crystal structures of three more cyclic ether complexes to provide additional information on these interesting systems. Each was made from anhydrous starting materials in AnalaR methanol.[5]

Complex (I): sodium bromide with 2,3 : 11,12-dibenzo-1,4,7,10,13,16-hexaoxocyclo-octadeca-2,11-diene. *Crystal data*: $\mathrm{C_{20}H_{24}O_6,NaBr,2H_2O}$. $M = 998\cdot8$, monoclinic, $a = 10\cdot558(6)$, $b = 13\cdot036(9)$, $c = 30\cdot677(18)$ Å, $\beta = 103\cdot2(0\cdot1)°$, $Z = 8$, two formula units per asymmetric unit; space group $P2_1/c$. 2880 diffractometer observations, final R value 0·083.

The asymmetric unit consists of two sodium–cyclic ether complexes, two bromide ions, and four water molecules. As shown in Figure 1, the conformation of both complexed ethers is similar to that found previously, but in one, Complex B, the sodium is further co-ordinated by two water molecules and in the other, Complex A, by one water molecule and one bromide ion. The remaining water molecule and bromide ion of the asymmetric unit do not co-ordinate with sodium but take part in a hydrogen-bonded chain which contains both solvent-separated and complexed ion pairs. In Complex B, the sodium ion is 0·07 Å from the plane of the ether-oxygen atoms and the Na–O distances range from 2·63—2·82 Å with an average of 2·71 Å. In Complex A the sodium ion is pulled out of the plane by 0·27 Å towards the bromide ion and this attraction results in a greater variation of Na–O, 2·54—2·89 Å, with an average of 2·73 Å These distances are similar to those found previously and are all larger than the three sodium–oxygen(water) distances of 2·31, 2·27, and 2·35 Å which are normal.[4]

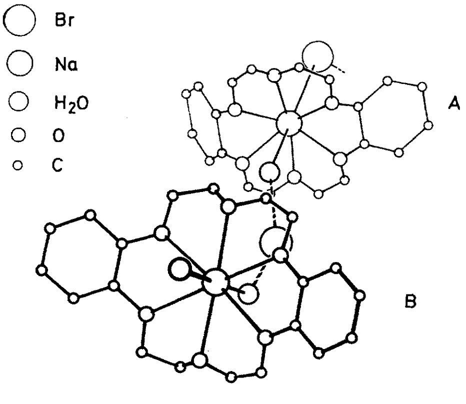

FIGURE 1. *The asymmetric unit of* (I), NaBr(*dibenzo*-18-*crown*-6), $2H_2O$. *Broken lines indicate hydrogen bonds between water molecules and bromide ions. The fourth water molecule in the asymmetric unit is not shown; it can be visualised as behind the bromide of Complex A or in front of the nearer water molecule of Complex B.*

Complex (II): sodium iodide with benzo-15-crown-5 (systematically named 2,3-benzo-1,4,7,10,13-pentaoxo-cyclopentadec-2-ene). *Crystal data*: $C_{14}H_{20}O_5$,NaI,H_2O. M = 436·3, orthorhombic, a = 12·271(4), b = 9·550(4), c = 15·719(5) Å, Z = 4, space group $P2_12_12_1$. 887 diffractometer observations, final R value 0·048.

The five ether-oxygen atoms are approximately coplanar; their average distance to sodium is 2·39 Å with a range of 2·35—2·43 Å. The sodium ion lies 0·75 Å out of this plane towards a water molecule (Na–O = 2·29 Å) which completes the pentagonal pyramidal configuration shown in Figure 2. The iodide ion is hydrogen-bonded to two symmetry-related water molecules and does not interact with the metal.

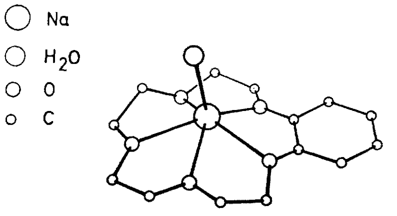

FIGURE 2. *The complex cation of compound* (II), NaI(*benzo*-15-*crown*-5),H_2O.

Complex (III): potassium iodide with dibenzo-30-crown-10 (systematically named 2,3:17,18-dibenzo-1,4,7,10,13,16,-19,22,25,28-decaoxocyclotriaconta-2,17-diene). *Crystal data*: $C_{28}H_{40}O_{10}$,KI. M = 702, orthorhombic, a = 19·576(6), b = 12·405(6), c = 12·965(4), Z = 4, space group *Pnna*. 1102 diffractometer observations, present R value 0·052.

The potassium complex and iodide ion lie on a crystallographic 2-fold axis indicated in Figure 3. The potassium ion is enclosed in a co-ordination sphere formed by the ten ether-oxygen atoms and, unlike the previous structures, there are no interactions other than those from the ligand. The molecular configuration is similar to that[6] of the potassium thiocyanate complex with nonactin, a cyclic antibiotic. The ten K–O distances range from 2·85—2·92Å with an average of 2·88 Å; these are normal for ten-coordinate potassium.

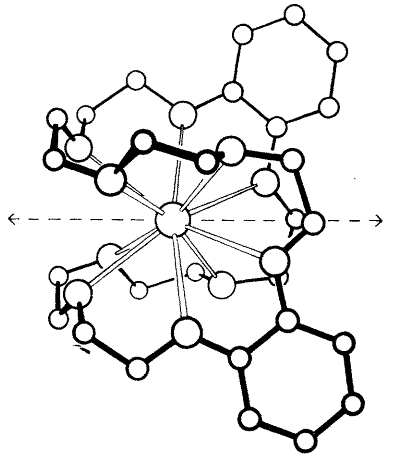

FIGURE 3. *The complex cation of compound* (III), KI(*dibenzo*-30-*crown*-10).

The structural data on cyclic ether complexes so far suggest that, whereas the large ring systems can completely replace the hydration sphere of the alkali metal, the small rings can do so only partially and with addition interactions from anions or water molecules. The accessibility of the complexed cation to additional ligands probably accounts for the variation of selectivity with the anion and solvent used [7]

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