Complexes of Alkali Metal Salts with Bridged Macrocyclic Polyethers; *X*-Ray Crystal Structure of (1,4,7,14,17,20,28,35-Octaoxa$[2^{3,29}\cdot2^{18,34}][7\cdot7]$-orthocyclophane)potassium Chloride Multihydrate†

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Summary The bridged macrocyclic polyether (**1b**) having 9 donor oxygen atoms forms water soluble complexes of 1 : 1 stoicheiometry with potassium and caesium salts, however polyethers (**1a**) and (**2a**) with 8 donor oxygen atoms, having shorter bridges, give 1 : 2 complexes with caesium chloride while maintaining 1 : 1 complexes with potassium salts; in the crystalline form of a typical 1 : 1 complex, KCl·(**2a**)·*n*(H_2O), there are discrete cations containing a potassium ion co-ordinated only by the encapsulating ligand while the chloride ions and water molecules (*n* is *ca.* 5) occupy disordered sites in columns.

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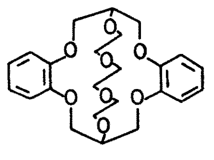
† The cyclophane nomenclature system (see F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847) has been used to name this compound in view of difficulties in extending the type of nomenclature used in ref. 1 for compounds (**1a**) and (**1b**) to systems such as (**2**) containing a further fused benzene ring.

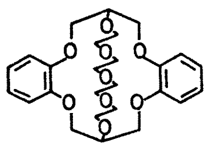
SOME members (**1a,b**) of a series of novel bridged macrocyclic polyethers have been shown to have high formation constants (up to 10^5 l mol^{-1}) for **1** : **1** complexes with alkali metal cations in aqueous solution[1] without the pH sensitivity characteristic of cryptates.[2] The series has been extended by synthesis of aromatic derivatives of (**1a**), *viz.* (**2a,b**), which are crystalline solids giving satisfactory elemental analyses. Formation constants measured in methanol for potassium and caesium bromides are shown in the Table; these indicate a **1** : **1** complex with potassium encapsulated for all the compounds and a **1** : **1** complex for caesium with the compound having a larger cavity, (**1b**), but **1** : **2** complexes with the compounds which space filling models indicate to be too small to accommodate this ion.

TABLE. Formation constants for alkali metal bromides in methanol at 25 °C: K_1 (l mol^{-1}) = $[M^+L]/[M^+][L]$, β_2(l^2 mol^{-2}) = $[M^+L_2]/[M^+][L]^2$ (accuracy 3%).

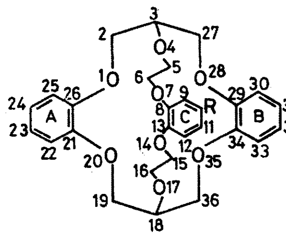
	K+	Cs+	
Ligand	K_1	K_1	β_2
(**1a**)	$3{\cdot}03 \times 10^7$	$4{\cdot}6 \times 10^4$	$3{\cdot}8 \times 10^7$
(**2a**)	$5{\cdot}7 \times 10^8$	$1{\cdot}8 \times 10^4$	$5{\cdot}0 \times 10^7$
(**2b**)	$6{\cdot}9 \times 10^8$	$2{\cdot}0 \times 10^4$	$9{\cdot}0 \times 10^7$
(**1b**)	$3{\cdot}3 \times 10^7$	$3{\cdot}3 \times 10^7$	—



(1a)



(1b)



(2)

a, R = H; b, R = Bu^t

The bridged macrocyclic polyethers have a very low solubility in water, while their complexes with alkali metal salts are much more soluble; this led us to expect that some of this solvent would be co-ordinated to the cation in the crystalline complexes which have several molecules of water of hydration. It has proved difficult to determine the exact number from conventional elemental analysis‡ or from the molecular weight determined from the density of the crystal and the volume of the unit cell. However, the crystal structure determination of a typical complex (1,4,7,14,17,20,28,35-octaoxa[$2^{3,29}{\cdot}2^{18,34}$][7·7]orthocyclophane)potassium chloride multihydrate,† KCl·(**2a**)·*n*(H_2O), has shown that *n* is *ca.* 5 and non-stoicheiometric; the water molecules and chloride ions are disordered, giving hydrogen-bonded anionic columns between which are discrete [K·**2a**]$^+$ cations (Figure).

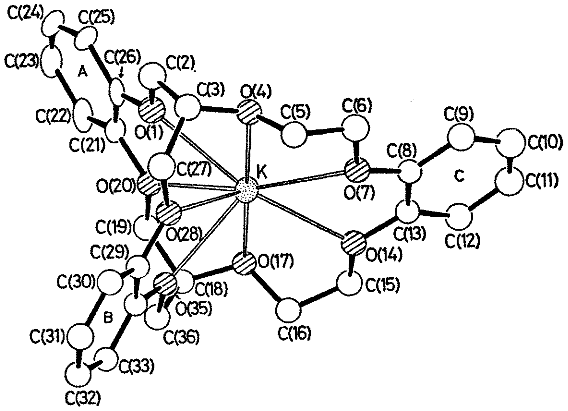


FIGURE. Structure of the cation [K·**2a**]$^+$. The K atom and atoms of the benzene ring A were refined with anisotropic vibration parameters.

Crystal data: $C_{28}H_{30}ClKO_8\cdot n(H_2O)$, $M = 659{\cdot}2$ ($n = 5$), monoclinic, $a = 22{\cdot}578(6)$, $b = 17{\cdot}162(5)$, $c = 16{\cdot}742(5)$ Å, $\beta = 99{\cdot}48(2)°$, space group $I2/c$ (non-standard setting of $C2/c$), $D_m = 1{\cdot}35(1)$ g cm^{-3}, $Z = 8$, D_c ($n = 5$) $= 1{\cdot}368$ and D_c ($n = 4{\cdot}5$) $= 1{\cdot}349$ g cm^{-3}. Measurements on an Enraf-Nonius CAD-4 diffractometer with Mo-$K_{\bar{\alpha}}$ radiation yielded 2137 observations having $|F| > 2\sigma_I$. The atoms of the complex cation have been located unequivocally; those of a disordered network of anions and water molecules have been obtained from difference electron density syntheses. The current value of R is 0·103.§

All eight oxygen atoms of the ligand are co-ordinated to the potassium atom (K–O, 2·68—2·74 Å), the four in the bridge, O(4), O(7), O(14), and O(17), and two catechol oxygen atoms, O(1) and O(20), form a ring nearly coplanar with the cation, while the other two oxygen atoms O(28) and O(35), on ring B, are 2·4 Å from this plane on the same side of the potassium ion. This ion has no neighbours within 3·65 Å on the other side and is certainly not co-ordinated by solvent or anion in the crystal. The geometry about the potassium atom differs from that provided by 8-donor atom [222] cryptate[3] because the bridgehead atoms, C(3) and C(18), are not colinear with, or co-ordinated to, the cation.

In the complex all the torsion angles are *ca.* 60° about the C–C bonds (apart from 0° at the benzene rings) and 180° about the C–O bonds [apart from one each about O(4)–C(3) and O(17)–C(18)]. The angles between the normals to the benzene rings and the normal to the plane through

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‡ *E.g.*, found: C, 51·66; H, 5·30; Cl, 5·13%; $C_{28}H_{30}O_8KCl\cdot n(H_2O)$ ($n = 5$) requires C, 51·02; H, 6·12; Cl, 5·38%; $n = 4{\cdot}5$ requires C, 51·73; H, 6·05; Cl, 5·45%.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the six oxygen atoms are 34° to A and 40° to C (and 74° between A and C). These are similar to the values found for 1:1 complexes of dibenzo-18-crown-6[4] and its tetramethyl derivative.[5] It is probable that the 1:2 complex formed with caesium would have a similar configuration to that found for the same stoicheiometry in tetramethyldibenzo-18-crown-6,[5] *i.e.* with the corresponding angles reduced to 15° giving a flatter molecule forming a sandwich complex.

There are no distances corresponding to potential hydrogen bonds between the anion–solvent columns and the oxygen atoms of the ligand. Within these columns are two peaks corresponding approximately to half occupied sites for chloride ions, the occupation of the remaining sites for water molecules varies from $^1/_3$ to $^2/_3$ giving a total of $n = ca.\ 5$ (with the isotropic vibration parameters fixed at 0·25 Å^2 the sum of the occupation numbers yielded $n = 5{\cdot}2$). There are more hydrogen atoms than possible hydrogen-bonded distances so their arrangements in the disordered networks cannot be assigned.

The i.r. spectrum shows a strong broad absorption around 3200—3600 cm^{-1} consistent with the presence of non-co-ordinated water molecules and the whole is similar to spectra of complexes of this ligand with potassium bromide, potassium thiocyanate, and sodium thiocyanate (all hydrated), suggesting that the conformation of the bicyclic molecule is the same and that the water molecules are not co-ordinated. From the i.r. spectrum a different conformation is to be expected for the free ligand.

The discovery that the water molecules are not co-ordinated led to alternative methods of obtaining crystalline 1:1 complexes, such as the use of large molecules of solvation, *e.g.* naphthalene-2,3-diol, or large anions which are not hydrogen bond acceptors, as in $KBPh_4$·(**1a**); the 1:2 complexes have not yet been isolated in a pure state.

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