Complex Formation between Dibenzo-3*n*-crown-*n* Ethers and the Diquat Dication

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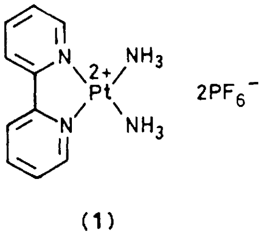
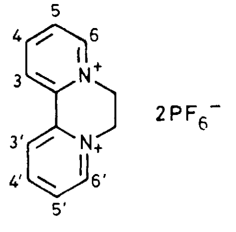
An *X*-ray crystallographic investigation of the complex between the diquat dication and dibenzo-30-crown-10, [Diquat.DB30C10][PF_6]$_2$, reveals gross structural features for host–guest complexes (I) and (II) in which weak [C–H · · · O] hydrogen bonding and charge transfer are the major components of host–guest binding; these same components are also responsible for the formation of stable and ordered 1 : 1 solution complexes between dibenzo-3*n*-crown-*n* (*n* = 9—12) and diquat bis(hexafluorophosphate) (**2**).

The observation[1,2] that [Pt(bipy)(NH_3)$_2$][PF_6]$_2$ (**1**) (bipy = 2,2′-bipyridine) forms stable complexes with dibenzo-crown ethers of the general type dibenzo-3*n*-crown-*n* (DB3*n*C*n*), where *n* = 7—12 in solution, and where *n* = 8, 10, and 11 in the solid state, prompted us to ask if organic bipyridinium dications would also behave as guest species towards this series of crown ethers.[3] We now describe how the diquat dication,[4] as its bis(hexafluorophosphate) salt[5] (**2**), is encapsulated by DB30C10 in the solid state and how it forms stable 1:1 complexes with DB3*n*C*n* (*n* = 9—12) hosts[†] in solution.

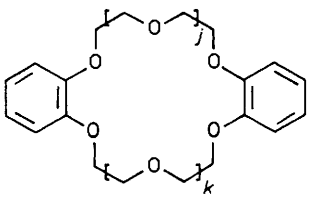
Diquat bis(hexafluorophosphate) (**2**) and dibenzo-crown ethers dissolve separately in organic solvents such as Me_2CO and MeCN giving colourless 0.001–0.01 M solutions which assume an orange-yellow colour on mixing. More dramatically, diquat bis(hexafluorophosphate) (**2**), sparingly soluble in CH_2Cl_2, is solubilised in this solvent by the addition of 1 mol. equiv. of DB30C10 to the extent that a 0.1 M solution, exhibiting an intense red colour, can be achieved. The colours are attributed to charge transfer between the electron-rich catechol units of the dibenzo-crown ethers and the electron-deficient bipyridinium ring system of the diquat dication. In support of this hypothesis, a very weak (ϵ 18) absorption for (**2**) with λ_{max} 425 nm in MeCN is enhanced on addition of 1 mol. equiv. of a dibenzo-crown ether. Figure 1 shows that this effect is a maximum for DB30C10. At the same molar concentration in MeCN, a 1:1 mixture of (**2**) and DB30C10 has an absorbance *ca.* 20 times greater than that of (**2**) alone. Red crystals of (**2**).DB30C10 with 1:1 guest–host stoicheiometry and suitable for *X*-ray structural investigation (Figures 2 and 3) were obtained from CH_2Cl_2–MeOH-n-C_7H_{16}.[‡] This investigation permits the following observations: (i) The two independent complexes (I and II) present in the asymmetric unit differ slightly in the conformations of their respective polyether chains, the relative dispositions of O(3) and O(13) constituting the most significant differences amidst wide-



(**1**)



(**2**)



DB3*n*C*n*	*j*	*k*
DB18C6	1	1
DB21C7	2	1
DB24C8	2	2
DB27C9	3	2
DB30C10	3	3
DB33C11	4	3
DB36C12	4	4

[†] DB18C6 (ref. 3) and DB24C8 (ref. 3) were obtained from Aldrich. DB21C7 (ref. 3), DB27C9, DB30C10 (refs. 1 and 3), DB33C11, and DB36C12 (ref. 1) were synthesised from the monobenzyl ether (J. Druey, *Bull. Soc. Chim. Fr.*, 1935, 1737) of 1,2-dihydroxybenzene and the appropriate (*i.e.* di-, tri-, tetra-, or penta-) poly-ethyleneglycol bistoluene-*p*-sulphonates (J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, 1972, **26**, 1471) by a stepwise procedure (*cf.* ref. 1). The compositions of all new compounds were confirmed by elemental analyses. Constitutional assignments were based upon the results of mass spectrometry and ^{1}H n.m.r. spectroscopy.

[‡] *Crystal data:* $C_{28}H_{40}O_{10}.C_{12}H_{12}N_2.P_2F_{12}.CH_3OH$, $M = 1042.83$, monoclinic, space group $P2_1/c$, $a = 11.369(1)$, $b = 22.218(5)$, $c = 37.663(8)$ Å, $\beta = 92.87(1)°$, $U = 9502$ Å^3, $Z = 8$ (two independent sets of complexes in the asymmetric unit), $D_c = 1.46$ g cm^{-3}. As the crystals desolvate rapidly on removal from solution, a single crystal was transferred under solution into a Lindemann glass capillary tube. Excess of solution was carefully drawn off and the tube was sealed leaving a small drop at one end of the tube to maintain a solvent vapour pressure. Data were obtained using Cu-K_α radiation (graphite monochromator) on a Nicolet R3m diffractometer. A total of 9772 independent reflections were measured ($\theta \leqslant 50°$) using the ω-scan measuring routine. Of these, 5549 had $|F_o| > 2.5\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically to $R = 0.14$. The high R factor is a consequence of disorder both in portions of the two macrocycles and in the four counterions. This is severe in the case of the hexafluorophosphate anions. Hydrogen atoms have not been allowed for at this stage because of program capacity limitations. (Their positions have been computed, however, on the basis of normal trigonal or tetrahedral geometries to permit analyses of possible hydrogen bonding interactions.) Nonetheless, the successful solution of this structure, comprising 136 non-hydrogen atoms in the asymmetric unit, illustrates the power and capabilities of a small dedicated computer and program system. (Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.) The atomic co-ordinates 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.

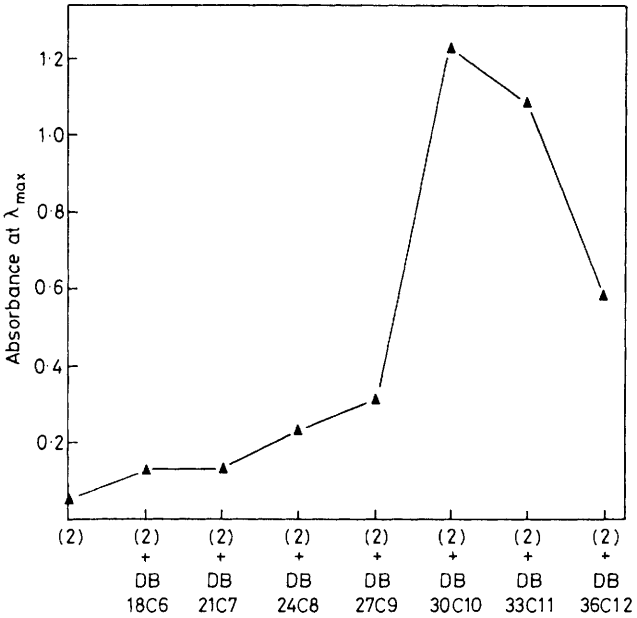


Figure 1. The dependence of the charge transfer band absorption intensities in the visible spectra of equimolar amounts (3×10^{-3} M, 1 cm cell) of (**2**) and the dibenzo crown ethers in MeCN upon the ring size of the macrocyclic hosts.

spread disorder as evidenced by the large thermal anisotropy of some of the atoms in the vicinity of these oxygen atoms. (ii) The disorder in the polyether chains may reflect the relatively weak nature of any [C–H ··· O] hydrogen bonding, which appears to be more pronounced for the aromatic hydrogen atoms at C(29), C(38), C(69), and C(78) on the pyridinium rings of the guest than for the hydrogen atoms in the bridging bismethylene unit.§ (iii) The phenolic oxymethylene units in DB30C10 are all nearly coplanar with the benzo-rings (*cf.* ref. 6), a conformational feature which (a) directs the phenolic oxygen lone-pair p-orbitals towards the nitrogen atoms of the diquat dication thereby permitting electrostatic bonding in the complexes, and (b) allows p–π overlap thereby enhancing charge transfer between the almost parallel π-electron-rich benzo-rings and the π-electron-deficient bipyridinium dication. The crystal structure of the 1 : 1 complex shows that, although the rigid guest dication assumes a structure very similar to that in crystalline diquat dibromide,[7] the highly flexible DB30C10 host adopts a conformation which is markedly different from that found in the solid state for the free crown.[8]

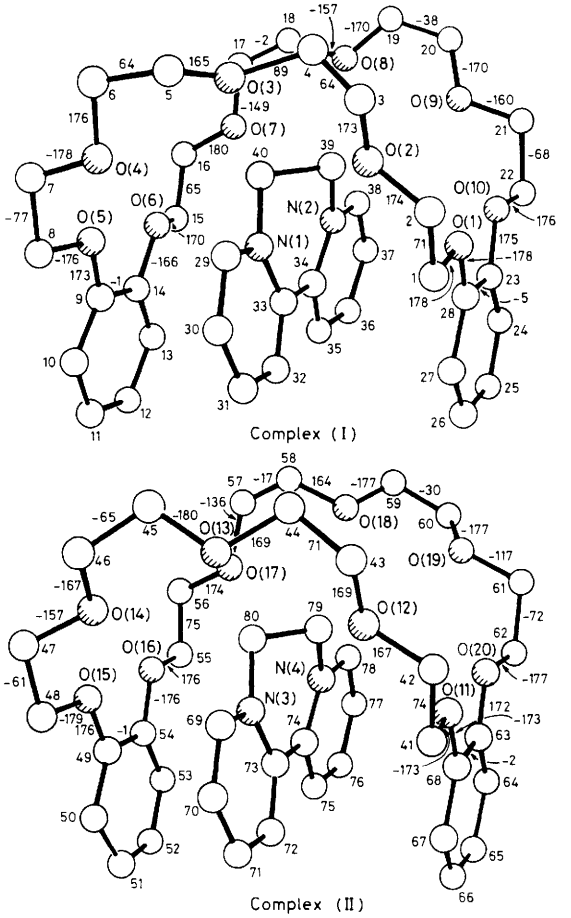


Figure 2. The solid state structures of the two independent complexes (I and II) in [Diquat–DB30C10]$^{2+}$. Torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 30-membered ring are shown beside the relevant C–C and C–O bonds in the structures. Selected hydrogen contact distances, R[C ··· O], R[H ··· O] (Å), angles (°) between COC planes and HO vectors, C–H ··· O angles (°) at H atoms assuming normal trigonal or tetrahedral geometry: [C(29)–O(4)], 2.99, [H(29)–O(4)], 2.22, 13, 136; [C(38)–O(8)], 3.23, [H(38)–O(8)], 2.34, 10, 154; [C(38)–O(9)], 3.13, [H(38)–O(9)], 2.39, 20, 133; [C(69)–O(14)], 3.10, [H(69)–O(14)], 2.48, 43, 122; [C(78)–O(18)], 3.22, [H(78)–O(18)], 2.33, 26, 155. Separation (Å) between pyridinium ring N in guest and phenolic O in host: N(1)–O(5), 3.28; N(3)–O(15), 3.35. Twist angles (°) between the pyridinium rings in the guest: 15 and 14 for complexes (I) and (II), respectively. Separation between the benzo rings in the host of 6.8 Å with 4° and 7° departures from parallel alignments of their mean planes in complexes (I) and (II), respectively.

Comparison of the ^{1}H n.m.r. spectra of equimolar mixtures of (**2**) and DB3nCn (n = 8—12), as solutions in CD_3COCD_3, with those for free diquat bis(hexafluorophosphate) (**2**) (*cf.* ref. 9 for assignments) and for the free benzo-crown ethers reveals (Figure 4) that when n = 10—12, there are dramatic upfield shifts for (i) H-3,3′, H-4,4′, and H-5,5′ of the guest and (ii) the aromatic protons of the hosts. The sign and magnitude of the shifts support a description of the 1 : 1 complex between (**2**) and DB3nCn (n = 10—12) in solution which is similar to that for the 1 : 1 complex between (**2**) and DB30C10 in the solid state. In such a structure, the considerable geometrical overlap between the aromatic units of the host and guest causes the anisotropic diamagnetic susceptibility of one aromatic system to reduce the local magnetic field which is experienced by ^{1}H nuclei attached to the other aromatic system. Additionally, the different nature of the spectra when n = 8 and 9 in DB3nCn hosts suggests that the complexes formed between (**2**) and DB24C8, and (**2**) and DB27C9 have solution structures different from those of the solid state complex formed between (**2**) and DB30C10.

Evidence for the stoicheiometry of the solution complexes, together with measurements of their association constants (K_a) and derived free energies of complexation ($\Delta G°$) for the equilibria (1) were obtained from a treatment (*cf.* ref. 10) of

$$[\text{Diquat}][\text{PF}_6]_2 + \text{DB3}n\text{C}n \rightleftharpoons [\text{Diquat.DB3}n\text{C}n][\text{PF}_6]_2 \qquad (1)$$

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§ In relation to this observation, base-catalysed deuterium exchange studies on *N*-methylpyridinium iodide indicate (K. W. Ratts, R. K. Howe, and W. G. Phillips, *J. Am. Chem. Soc.*, 1969, **91**, 6115) that the hydrogen atoms on C(2) and C(6) of the pyridinium ring are more acidic than those in the *N*-methyl group.

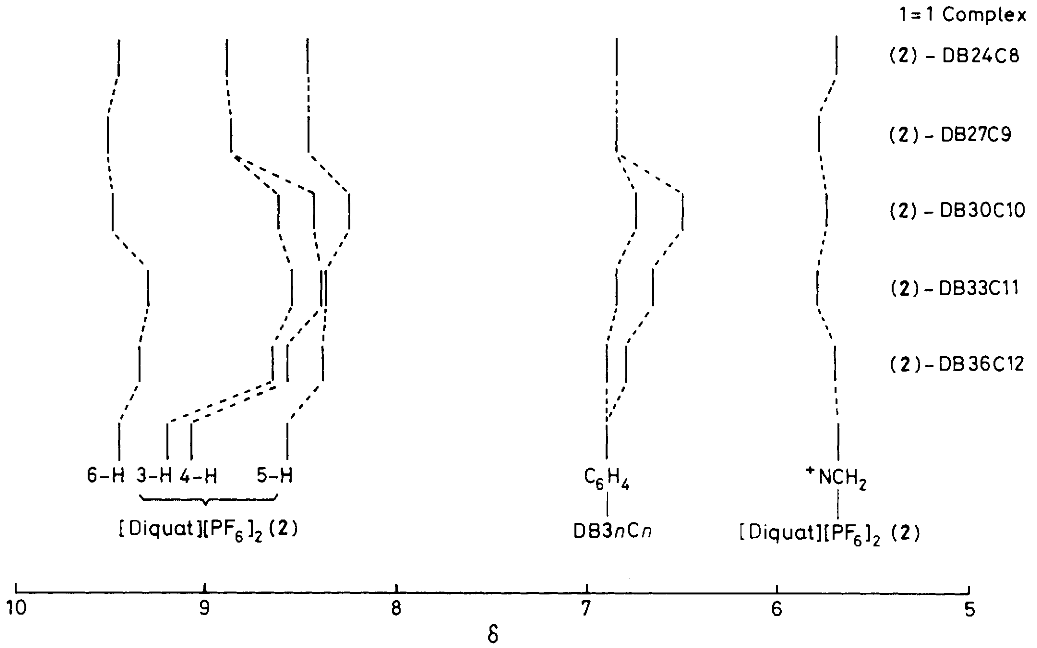

Figure 4. Partial ^{1}H n.m.r. line spectra of equimolar amounts of (**2**) and the dibenzo crown ethers from DB24C8 to DB36C12 in CD_3COCD_3 compared with those of (**2**) and the free hosts.

the dependence on concentrations of the absorption bands at 400 nm for 1 : 1 mixtures of (**2**) and DB3nCn. Assuming 1 : 1 complexation between host and guest, it may be shown that equation (2) applies, where $A_C = A - \epsilon_D dl$, $\epsilon_C = \epsilon_X - \epsilon_D$, A is the measured absorbance, ϵ_D is the extinction coefficient for diquat, d is the concentration of both diquat and DB3nCn, l is the path length, and ϵ_X is the extinction coefficient for the complex. Thus, a plot of d/A_C against $1/(A_C)^{\frac{1}{2}}$ should be linear with a slope of $1/(K_a\epsilon_C l)^{\frac{1}{2}}$ and an intercept of $1/\epsilon_C l$. In Me_2CO for n = 9—12 in the DB3nCn hosts, this relationship was obeyed and full regression analyses of the data in each case afforded the following results: for n = 9, 10, 11, and 12, respectively, K_a = 410, 17 500, 10 800, and 2 000 dm^3 mol^{-1} corresponding to $\Delta G^\circ = -3.6$, -5.8, -5.5, and -4.5 kcal mol^{-1} (1 cal = 4.184 J). Thus, the most stable 1 : 1 complex formed in Me_2CO by this range of hosts¶ is that involving DB30C10 which also happens to afford, most readily amongst the DB3nCn hosts examined, a crystalline 1 : 1 complex.

$$\frac{d}{A_C} = \frac{1}{(K_a\epsilon_C l)^{\frac{1}{2}}} \cdot \frac{1}{(A_C)^{\frac{1}{2}}} + \frac{1}{\epsilon_C l} \qquad (2)$$

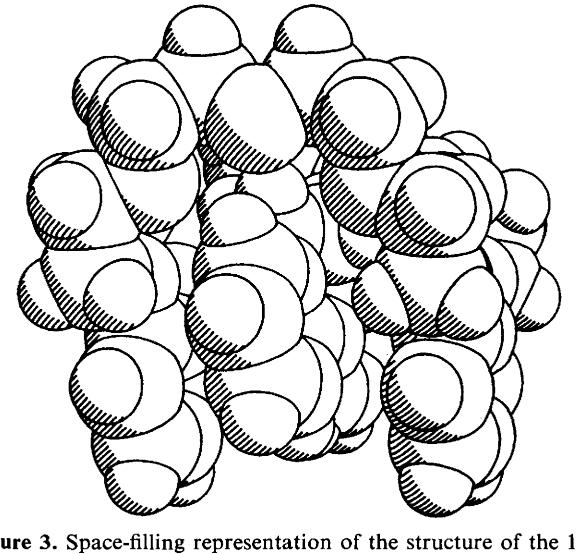

Figure 3. Space-filling representation of the structure of the 1 : 1 complex (II) formed between the diquat dication and DB30C10.

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¶ In the case of DB24C8, a complex of 2 : 1 (guest : host) stoicheiometry is believed to be formed in acetone with a K_a value of 390 000 dm^6 mol^{-2} ($\Delta G^\circ = -7.6$ kcal mol^{-1}) as shown by an independent method, *cf.* partial ^{1}H n.m.r. line spectrum of (**2**).DB24C8 in Figure 4.