

Synthesis, X-Ray Crystal Structure, and Reactivity of Ternary Complexes of Crown Ethers, Organic π -Acceptors, and Salts

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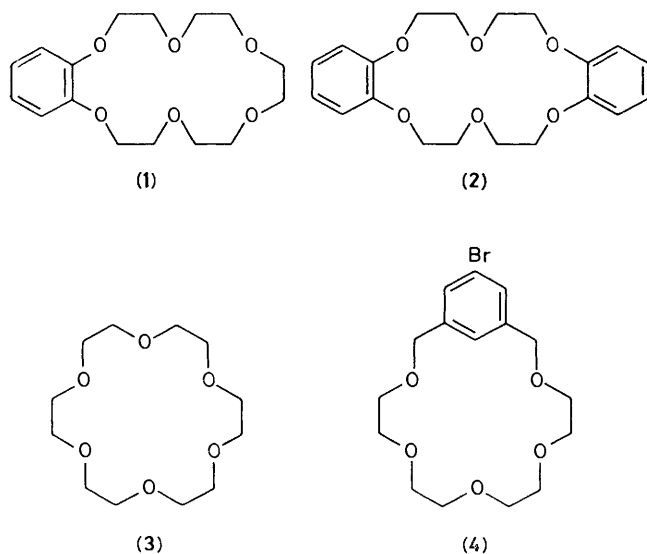
Single-crystal X-ray analysis of a stable ternary complex of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), dibenzo-18-crown-6 (**2**), and *t*-butylammonium perchlorate reveals a close contact between the anion and DDQ; in similar ternary complexes of crown ethers, tetracyanoethylene (TCNE), and halides a one-electron transfer is observed.

The mimicry of enzyme-catalysed reactions by synthetic macrocyclic polyethers has been reported in several recent publications.¹ Both Chao and Cram,² and Lehn and Sirlin³ have found rate enhancement and enantiomeric differentiation in transacylation reactions of amino-acid *p*-nitrophenyl esters catalysed by chiral crown ethers bearing mercapto-groups.

Mimicry of NAD(P)H by macrocyclic polyethers with built-in dihydropyridine moieties has been described by Kellogg *et al.*⁴ and by Behr and Lehn.⁵ In both cases the

reactions were proved to occur in binary complexes of crown ether and substrate. The transacylation reactions take place with solvent molecules as the reagent and in the hydrogen-transfer reactions the reacting dihydropyridine is covalently bound to the macrocycle. Ideally a crown ether should bind both the substrate and the reagent reversibly to form a ternary complex. In this communication we report ternary complexes of crown ethers, organic π -acceptors, and salts.

Studying the co-operative interaction of *t*-butylammonium perchlorate and tetracyanoethylene (TCNE) with benzo-18-



crown-6 (1) we found that the blue charge-transfer absorption present in chloroform solutions of (1) and TCNE,[†] with $\lambda_{\max} = 580$ nm, is absent in solutions containing the complex of (1)-Bu^tNH₃ClO₄ and TCNE.

When Bu^tNH₃ClO₄ was added to a chloroform solution of the charge-transfer complex of dibenzo-18-crown-6 (2) and TCNE, we also observed the complete disappearance of the blue colour with $\lambda_{\max} = 590$ nm. However, this was accompanied by the precipitation of red crystals (decomp. 143–144 °C to a liquid and a solid, m.p. 178–180 °C)[‡] from the solution. Elemental analysis showed that this material had a molecular composition corresponding to equimolar amounts of salt, TCNE, and (2). The same type of crystalline ternary complex was obtained by the treatment of the (2)-Bu^tNH₃ClO₄ complex with an equimolar amount of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in chloroform.[‡] The structure of this complex, m.p. 177–178 °C, at 143 K has now been determined by *X*-ray analysis.

Crystal data: C₃₂H₃₆Cl₃O₁₂N₃, orthorhombic, space group *Pbca*, $a = 31.66(2)$, $b = 15.546(3)$, $c = 14.358(5)$ Å, $Z = 8$; 3976 reflexions with $I > \sigma(I)$ (counting statistics) were measured (Philips PW1100 diffractometer, ω - 2θ scan mode, Cu- K_{α} radiation, graphite monochromator, $3 < \theta < 60^{\circ}$). The structure was solved by direct methods[§] and refined to a final *R*-factor of 14.1%, using isotropic thermal parameters for the non-hydrogen atoms.[§] The resulting crystal structure is shown in Figure 1. The structure can be described as a packing of two types of columns with opposite charge. The first type contains DDQ molecules and perchlorate ions. In the second type alternating t-butylammonium ions and crown ether molecules are found. Although no hydrogen atoms have been located yet, it is clear that the t-butylammonium ion is bound to the crown ether by N-H...O hydrogen bonds and electrostatic N⁺...O interactions.

[†] Krishnan *et al.* have reported charge-transfer complexes of benzo-crown ethers with TCNE⁶ and DDQ⁷ giving absorption bands in the region 580–620 and 570–700 nm, respectively. We have determined the association constants of the complexes of (1)-TCNE ($K = 2.6$ l mol⁻¹, $\epsilon = 709$ l mol⁻¹ cm⁻¹) and (2)-TCNE ($K = 4.5$ l mol⁻¹, $\epsilon = 899$ l mol⁻¹ cm⁻¹).

[‡] Satisfactory elemental analyses were obtained.

[§] 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.

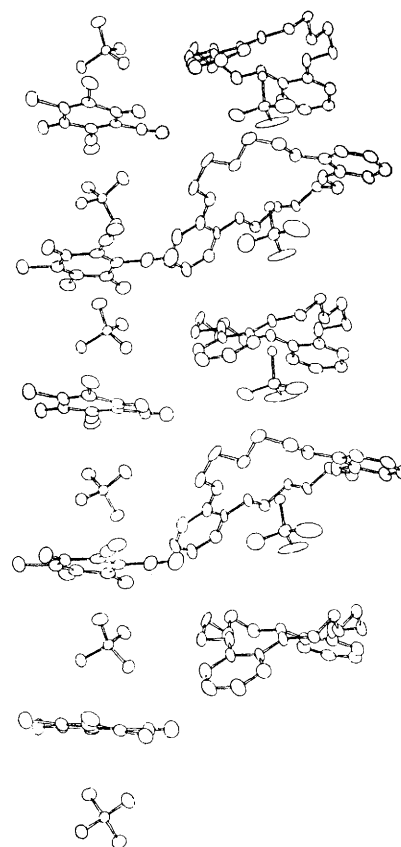


Figure 1

Knowing the structure in the solid state it is possible to rationalize why the blue charge-transfer absorption is absent in such ternary complexes. It is also possible that in solution the π -electron acceptor has virtually no interaction with the π -donating aryl rings of the dibenzo-18-crown-6 but is interacting with the perchlorate anions (*vide infra*). The binding of the t-butylammonium cation to the macrocyclic polyether ring is likely to be of the same type as found in the corresponding complex of Bu^tNH₃PF₆ with the 18-crown-5 ether (4).⁹

Attempts to prepare similar ternary complexes with nucleophilic anions such as Br⁻, Cl⁻, and F⁻ led to different results. Treatment of the dark blue solutions containing equimolar amounts of TCNE and (2) in chloroform with Bu^tNH₃Br or with KBr caused a colour change from blue to red with $\lambda_{\max} = 460$ nm in the u.v. spectrum. In view of the positions of the perchlorate anion and DDQ in the ternary complex we assign this absorption to a charge-transfer band of a complex of TCNE with the bromide anion.[¶] This was confirmed by an experiment in which 18-crown-6 (3), which cannot form a π -charge-transfer complex with TCNE, replaced (2). We obtained a red solution exhibiting the same absorption at 460 nm in the u.v. spectrum. Similarly, solutions of 18-crown-6 and the corresponding potassium chloride or fluoride salts showed absorptions with $\lambda_{\max} = 400$ nm. The result with the chloride salt differs from that reported by Tada *et al.*¹¹ who found that the charge-transfer absorption band of the (2)-TCNE complex shifts to lower wavelength by only 20 nm upon addition of one equivalent of KCl to a solution of the complex in acetonitrile containing 20% of water. All solutions of TCNE, crown ether, and Br⁻, Cl⁻, or

[¶] Briegleb *et al.*¹⁰ have reported a charge-transfer absorption at 460.8 nm for the LiBr-TCNE complex in acetonitrile.

F⁻ salts in chloroform showed strong e.s.r. signals corresponding to the spectrum of the TCNE anion radical.¹² This indicates complete electron transfer from the halide anions to TCNE. Line-broadening, dependent on the concentration of TCNE, was observed indicating exchange between TCNE and the TCNE anion radical.¹³

In the presence of water and oxygen the TCNE anion radical reacted slowly to give almost exclusively the tricyanoethenolate anion, isolated as the t-butylammonium tricyanoethenolate crown ether complex.¹⁴ The structure of this complex was confirmed by independent synthesis of the complex of (3) and t-butylammonium tricyanoethenolate.^{15†**}

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** The (3)-Bu^tNH₃(CN)₂C=C(CN)O⁴ complex was obtained by equilibration of an aqueous solution of tricyanoethenol and Bu^tNH₃Cl with a chloroform solution of (3). After separation of the two layers and drying of the organic layer diethyl ether was added. The complex of (3) and Bu^tNH₃(CN)₂C=C(CN)O precipitated, m.p. 104–105 °C.

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