

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

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Benzo- and dibenzo-18-crown-6 (1) and (2) form charge-transfer complexes with tetracyanoethylene (TCNE) in chloroform with association constants of 2.6 ± 0.2 and $4.5 \pm 0.4 \text{ l mol}^{-1}$. In the presence of 1 equiv. of t-butylammonium perchlorate ($\text{Bu}^t\text{NH}_3\text{ClO}_4$) a solid ternary complex of (2), TCNE, and $\text{Bu}^t\text{NH}_3\text{ClO}_4$ is formed. Single-crystal X-ray analysis of a similar ternary complex of (2), $\text{Bu}^t\text{NH}_3\text{ClO}_4$ and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) revealed the close proximity of the perchlorate anion and DDQ. Ternary complexes of TCNE, crown ethers (1)–(3), and salts with nucleophilic anions (Br^- , Cl^- , and F^-) react to give the TCNE^- radical anion as proven by e.s.r. spectroscopy. In the presence of water and/or oxygen 18-crown-6 (3), TCNE, and $\text{Bu}^t\text{NH}_3\text{Br}$ react to yield the 18-crown-6- $\text{Bu}^t\text{NH}_3(\text{NC})_2\text{C}=\text{C}(\text{CN})\text{O}$ complex.

Catalysis by enzymes is found in all kinds of biochemical processes. Enzymes bring substrates and reagents in close proximity, so that they can react easily to give the desired products. In this conversion, enzymes are extremely substrate selective. In order to acquire a similarly high degree of substrate selectivity and reactivity in reactions, a number of synthetic macrocyclic polyethers that mimic enzyme-type catalysis have been described recently. Van Bergen and Kellogg¹ have synthesized crown ethers that mimic the enzyme NAD(P)H. Enhanced rates of reactions have also been reported by Behr and Lehn² for hydrogen transfer of dihydropyridine to pyridinium in crown ether complexes, for thiolysis in complexes with macrocyclic molecules by Lehn and Sirlin,³ and for transacylations of amino ester salts by Chao and Cram.⁴ In the latter reactions in addition to catalysis of the reaction enantiomeric differentiation by chiral crown ethers is observed.

However, in all these cases the reagent is either part of the crown ether, which means that during the reaction the 'enzyme' is consumed, or the solvent is reacting. It would be preferable to bring the substrate and reagent into close proximity in a ternary complex, in which the reagent is complexed by the crown ether in the usual way and the substrates are complexed by other forces such as charge-transfer complexation. Charge-transfer complexes of crown ethers and organic π -acceptors have been reported previously by Krishnan *et al.*⁵ In this paper ternary complexes of crown ethers, organic π -acceptors, and salts are described.

Results and Discussion

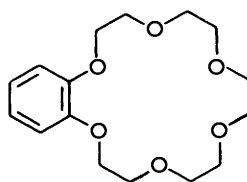
The π -acceptor tetracyanoethylene (TCNE) was found to form blue charge-transfer complexes with benzo-18-crown-6 (1) and dibenzo-18-crown-6 (2) with λ_{max} at 580 and 590 nm respectively (Figure 1) in chloroform.^{5,6} The association constants of these complexes, as is given by equation (1), have been determined in CHCl_3 at 20 °C, using u.v. spectroscopic data [equation (2)]. In equations (1) and (2) $[\text{AD}]$ is the

$$K = \frac{[\text{AD}]}{[\text{A}][\text{D}]} = \frac{[\text{AD}]}{([\text{A}]_0 - [\text{AD}])([\text{D}]_0 - [\text{AD}])} \quad (1)$$

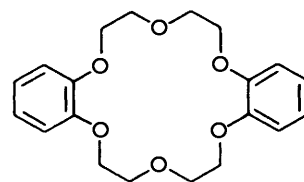
$$E = \epsilon[\text{AD}]l \quad (2)$$

Table. Association constants of (1) and (2) with TCNE in CHCl_3 at 20 °C

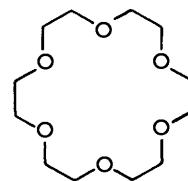
Crown ether	$K/\text{l mol}^{-1}$	$\epsilon/\text{l mol}^{-1} \text{ cm}^{-1}$
(1)	2.6 ± 0.2	709 ± 40
(2)	4.5 ± 0.4	890 ± 70



(1)



(2)



(3)

concentration of the charge-transfer complex, $[\text{A}]_{(0)}$ the (initial) concentration of the acceptor (TCNE), $[\text{D}]_{(0)}$ the initial concentration of the donor (crown ether), E the extinction, ϵ the molar extinction coefficient, and l the pathway in cm. Both the association constant K and ϵ are unknown, and consequently K has been determined by an iterative procedure, analogous to methods used for the determination of association constants of crown ether complexes; details are given in the Experimental section and the results are summarized in the Table.

Jayathirtha and Krishnan^{5a} have reported K values of 1.162 (24 °C) and 1.422 l mol^{-1} (11 °C) for the complexation of (2) with TCNE in CH_2Cl_2 . These values are in good agreement with our results, because the association constants tend to be lower in solvents with higher polarity.

A remarkable change of the u.v. spectrum of the charge-transfer complexes of TCNE with (1) and (2) was found in the presence of t-butylammonium perchlorate ($\text{Bu}^t\text{NH}_3\text{ClO}_4$).

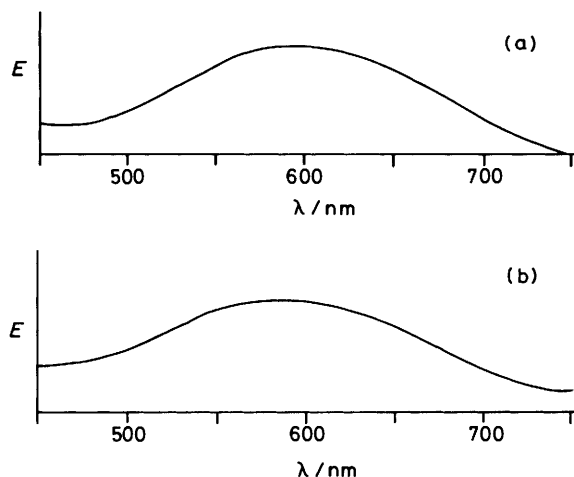


Figure 1. Parts of the u.v. spectra of the charge-transfer complexes of benzo-18-crown-6 (a) and dibenzo-18-crown-6 (b) with TCNE

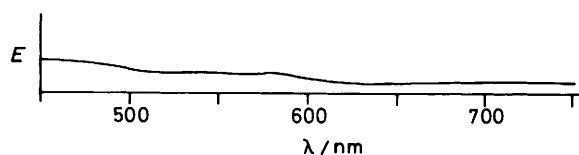


Figure 2. Parts of the u.v. spectra of a CHCl_3 solution containing benzo-18-crown-6, TCNE, and $\text{Bu}^4\text{NH}_3\text{ClO}_4$ in a 1:1:1 ratio

When the salt was added to a chloroform solution, containing benzo-18-crown-6 (1) and TCNE, the blue colour became less intense and vanished almost completely when the ratio of (1) and $\text{Bu}^4\text{NH}_3\text{ClO}_4$ was 1:1 (Figure 2). In the region where the individual components absorb [TCNE: $\lambda_{\text{max}}(\text{CHCl}_3)$ 267 and 276 nm; (1): $\lambda_{\text{max}}(\text{CHCl}_3)$ 245 and 278 nm; (1)· $\text{Bu}^4\text{NH}_3\text{ClO}_4$: $\lambda_{\text{max}}(\text{CHCl}_3)$ 243, 275, and 281 nm] the absorption band broadened.*

When $\text{Bu}^4\text{NH}_3\text{ClO}_4$ was added to a chloroform solution, containing the charge-transfer complex of dibenzo-18-crown-6 (2) and TCNE, complete disappearance of the blue colour also occurred, and this was accompanied by the precipitation of red crystals. Elemental analysis showed that this material had a molecular composition corresponding to equimolar amounts of salt, TCNE, and (2). The same type of ternary complex was obtained by treatment of the (2)· $\text{Bu}^4\text{NH}_3\text{ClO}_4$ complex with an equimolar amount of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in chloroform and the structure of this complex has been determined by X-ray analysis.

X-Ray Study of the (2)· $\text{Bu}^4\text{NH}_3\text{ClO}_4$ ·DDQ Complex.—The structure of the ternary complex (2)· $\text{Bu}^4\text{NH}_3\text{ClO}_4$ ·DDQ was solved by direct methods and refined to a final *R* factor of 8.9% using anisotropic thermal parameters for the non-hydrogen atoms.⁷ Most hydrogen atoms could be located in a difference-Fourier synthesis. The resulting crystal structure is shown in Figure 3. As is evident from Figure 3 the *t*-butylammonium ions exhibit a relatively large anisotropic thermal motion. Therefore not all hydrogens in this part of the molecule could be located. The structure can be described as a packing of two types of

columns with opposite charge. The first column contains DDQ molecules and perchlorate ions and the second column alternating *t*-butylammonium ions and crown ether molecules. As already mentioned the location of hydrogen atoms in the *t*-butylammonium ion is difficult. From the orientation of the *t*-butylammonium ion with respect to the crown ether however 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, and is likely to be of the same type as found in the corresponding complex of $\text{Bu}^4\text{NH}_3\text{PF}_6$ with *p*-bromo-1,3-xylyl-18-crown-5.⁸

Knowing the structure in the solid state it can readily be seen why the blue charge-transfer absorption is absent in such ternary complexes. It is very likely that also in solution the π -electron acceptor has virtually no interaction with the π -donating aryl rings of (di)benzo-18-crown-6 but it is interacting with the perchlorate anions.

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 $\text{Bu}^4\text{NH}_3\text{Br}$ or with KBr resulted in a colour change from blue to red with λ_{max} 460 nm in the u.v. spectrum (Figure 4). In analogy with the positions of the perchlorate anion and DDQ in the ternary complex this absorption was assigned 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, was used instead of (2). A red solution, exhibiting the same absorption at 460 nm in the u.v. spectrum, was obtained (Figure 4).

The dark blue colour of a chloroform solution, containing dibenzo-18-crown-6 (2) and TCNE in a 1:1 ratio, changed gradually to green upon addition of an equimolar amount of KCl or $\text{Bu}^4\text{NH}_3\text{Cl}$. This green colour was shown to be a combination of blue and yellow with absorptions at 400 and 590 nm (Figure 5). The absorption at 590 nm can be attributed to the charge-transfer complex of dibenzo-18-crown-6 and TCNE, and the absorption at 400 nm can be attributed to the charge-transfer complex of TCNE with the halide anion, as was proven by the interaction of 18-crown-6 and TCNE with $\text{Bu}^4\text{NH}_3\text{Cl}$ or KCl.

The results with the chloride salt differs from those reported by Tada *et al.*¹⁰ who found that the charge-transfer absorption band of the (2)·TCNE complex shifts to lower wavelength by only 20 nm upon addition of 1 equivalent of KCl to a solution of the complex in acetonitrile containing 20% water.

A solution of equimolar amounts of 18-crown-6, TCNE, and KF showed an absorption in the u.v. spectrum with λ_{max} 400 nm, which can be attributed to the charge-transfer complex of 18-crown-6 with the F^- anion.

All solutions of TCNE, crown ether, and halide salts in chloroform showed strong e.s.r. signals corresponding to the spectrum of the TCNE^- anion radical.¹¹ This indicates complete electron transfer from the halide anion to TCNE. Line-broadening, dependent on the concentration of TCNE, was observed indicating exchange between TCNE and the TCNE^- anion radical.¹² In Figure 6a the e.s.r. spectrum of a solution of 18-crown-6, TCNE, and KF (in a 1:1:1 ratio) in chloroform is shown. This spectrum shows a hyperfine structure of 15 line-broadened signals, indicating that besides the coupling with the four nitrogen atoms, the coupling with the ¹³C atoms (two types) is also observed. The spectrum was simulated (Figure 6b) using a_{N} 1.574, $a_{\text{C}(\text{CN})}$ 9.541, and $a_{\text{C}(\text{C}=\text{C})}$ 2.203, and taking into account the natural abundance of the ¹³C atoms.

* Krishnan and his co-workers have reported charge-transfer complexes of benzocrown ethers with TCNE^{5a} and DDQ^{5b} giving absorption bands in the region 580–620 and 570–700 nm, respectively, in methylene dichloride.

† Briegleb *et al.*⁹ have reported a charge-transfer absorption at 460.8 nm for the LiBr–TCNE complex in acetonitrile

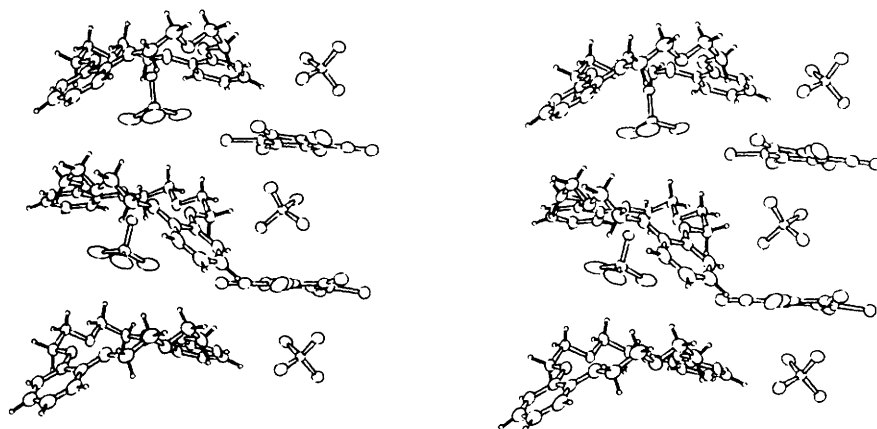


Figure 3. X-Ray structure of the dibenzo-18-crown-6-Bu'NH₃ClO₄-DDQ complex

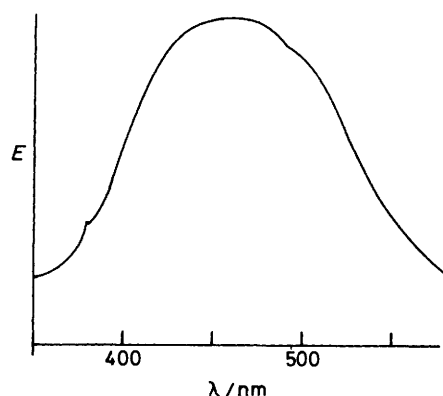


Figure 4. Parts of the u.v. spectra of a CHCl₃ solution containing benzo-18-crown-6 or 18-crown-6, Bu'NH₃Br, and TCNE in a 1:1:1 ratio

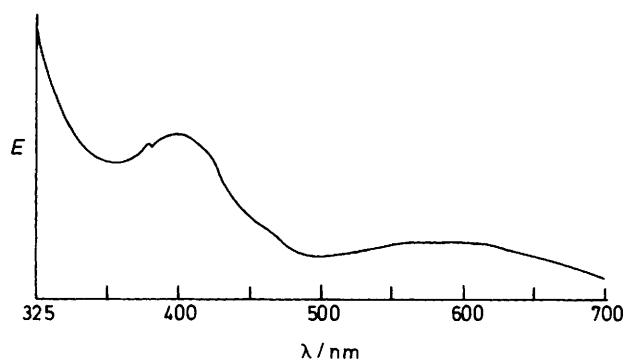


Figure 5. U.v. spectrum of a CHCl₃ solution containing dibenzo-18-crown-6, Bu'NH₃Cl, and TCNE in a 1:1:1 ratio

In the course of time the absorption due to the charge-transfer complexation of TCNE and the halide anions vanished almost completely (Figure 7a) and at the same time another absorption appeared with λ_{max} 300 nm (Figure 7b). It is known from the literature¹³ that the TCNE⁻ radical anion can be converted into the tricyanoethenolate anion (NC)₂C=C(CN)O⁻ in the presence of oxygen and water. Because of the presence of the TCNE⁻ radical anions in solution, due to complete electron transfer from the halide anions to TCNE, it can be assumed that in our experiments these radical anions were

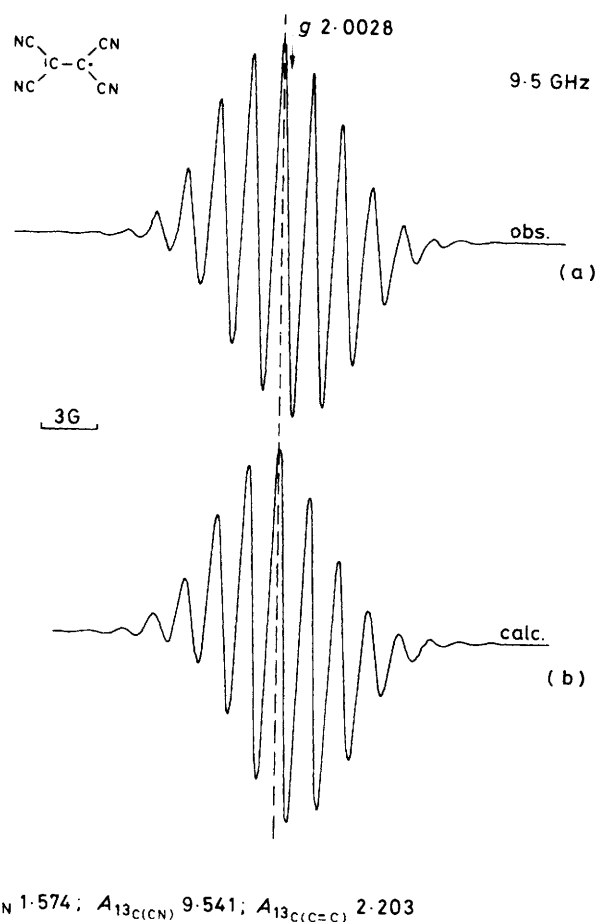


Figure 6. E.s.r. spectra of a CHCl₃ solution containing 18-crown-6, TCNE, and KF in a 1:1:1 ratio. (a) Experimental and (b) simulated

converted into the corresponding tricyanoethenolates by small amounts of water and oxygen present in the solvent. In the case of 18-crown-6, Bu'NH₃Br, and TCNE this was proven by isolation of the 18-crown-6-Bu'NH₃(NC)₂C=C(CN)O complex. When the absorption at 450 nm had completely vanished the complex could be precipitated from the solution by addition of diethyl ether. The structure of the complex was confirmed by independent synthesis of the complex of 18-crown-6 and t-butylammonium tricyanoethenolate. For this purpose a

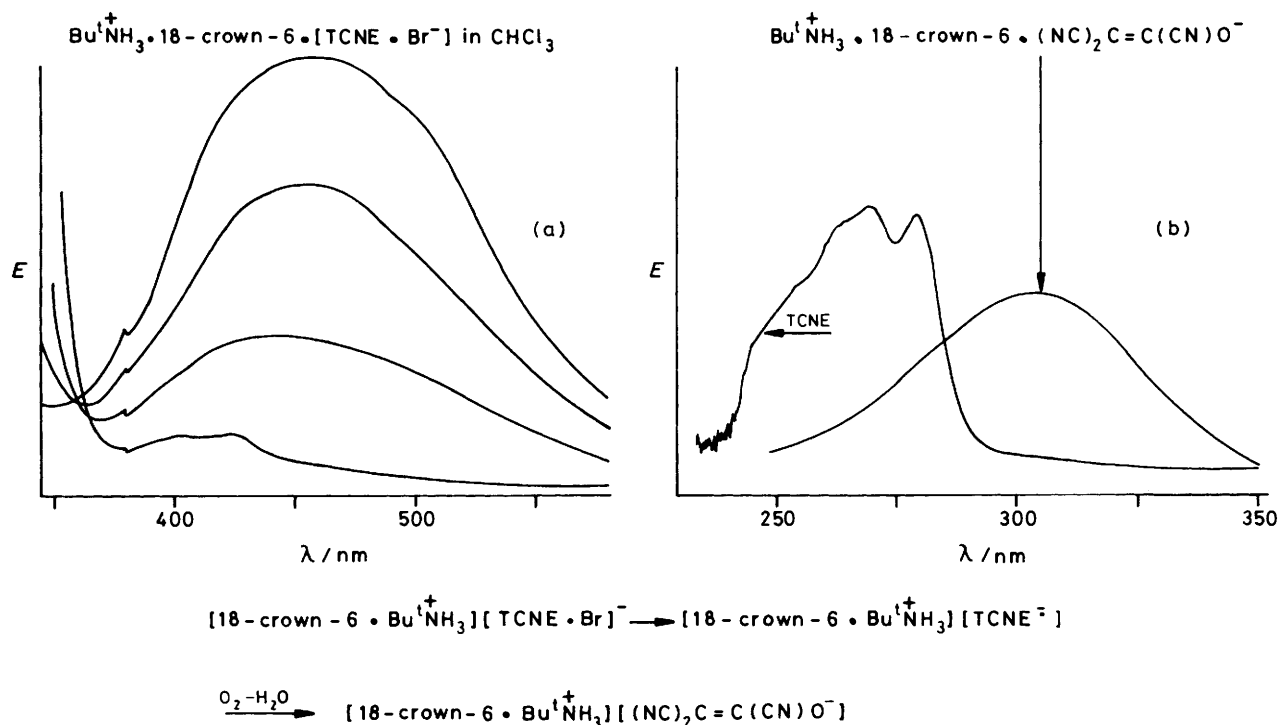


Figure 7. Time-dependent u.v. spectra of a CHCl_3 solution containing 18-crown-6, $\text{Bu}^+\text{NH}_3\text{Br}$, and TCNE in a 1 : 1 : 1 ratio

chloroform solution, containing 18-crown-6, was equilibrated with an aqueous solution containing equimolar amounts of $\text{Bu}^+\text{NH}_3\text{Cl}$ and tricyanoethanol.¹⁴ The 18-crown-6- $\text{Bu}^+\text{NH}_3(\text{NC})_2\text{C}=\text{C}(\text{CN})\text{O}$ complex was precipitated from the chloroform layer by addition of diethyl ether.

Conclusions.—Crown ethers, salts, and organic π -acceptors can form ternary complexes, in which the anion and the acceptor are in close contact. Dibenzo-18-crown-6, $\text{Bu}^+\text{NH}_3\text{ClO}_4$, and TCNE or DDQ form stable complexes in this way. In similar complexes of crown ethers, TCNE, and halide salts a one-electron transfer from the halide ion to TCNE is observed, giving the $\text{TCNE}^{\cdot-}$ radical anion. In the presence of water and oxygen the radical anion reacts slowly to give the tricyanoethenolate anion.

Experimental

General. M.p.s were determined with a Reichert apparatus and are uncorrected. Mass spectra were obtained with a Varian Mat 311A instrument. U.v. spectra were recorded with an SP 800 spectrophotometer. Numerical u.v. data were obtained with a Carl Zeiss PMQ II spectrophotometer. E.s.r. spectra were recorded with a Varian E-line EPR spectrometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis.

Materials.—TCNE and DDQ were sublimed before use. Benzo-18-crown-6¹⁵ (1), dibenzo-18-crown-6¹⁶ (2), and 18-crown-6¹⁷ (3) were synthesized according to known methods.

Dibenzo-18-crown-6- $\text{Bu}^+\text{NH}_3\text{ClO}_4$ -TCNE. The dibenzo-18-crown-6- $\text{Bu}^+\text{NH}_3\text{ClO}_4$ -TCNE complex precipitated from a CHCl_3 solution containing dibenzo-18-crown-6 (100 mg), $\text{Bu}^+\text{NH}_3\text{ClO}_4$ (50 mg), and TCNE (36 mg) giving red crystals (84%), m.p. 143–144 °C, decomposition to a liquid and a solid,

m.p. 178–180 °C; $\delta(\text{CD}_2\text{Cl}_2)$ 7.04 (s, 8 H, ArH), 4.36–4.00 (m, 16 H, OCH_2) and 0.92 (s, 9 H, CH_3); the mass spectrum showed the molecular ions of dibenzo-18-crown-6, m/e 360.16 (M^+ ; calc. 360.41), and of TCNE, m/e 128.01 (M^+ ; calc. 128.09) (Found: C, 51.0; H, 5.25; N, 9.7; Cl, 12.3. Calc. for $\text{C}_{30}\text{H}_{36}\text{ClN}_5\text{O}_{10} \cdot 0.5 \text{CHCl}_3$: C, 50.75; H, 5.1; N, 9.7; Cl, 12.3%).

Dibenzo-18-crown-6- $\text{Bu}^+\text{NH}_3\text{ClO}_4$ -DDQ. The dibenzo-18-crown-6- $\text{Bu}^+\text{NH}_3\text{ClO}_4$ -DDQ complex precipitated from a CHCl_3 solution containing dibenzo-18-crown-6 (100 mg), $\text{Bu}^+\text{NH}_3\text{ClO}_4$ (50 mg), and DDQ (63 mg) giving red crystals (76%), m.p. 177–178 °C; $\delta(\text{CDCl}_3\text{-}[^2\text{H}_6]\text{DMSO})$ 6.88 (s, 8 H, ArH), 4.16–3.94 (m, 16 H, OCH_2), and 1.29 (s, 9 H, CH_3); the mass spectrum showed the molecular ions of dibenzo-18-crown-6, m/e 360.16 (M^+ ; calc. 360.41), and DDQ, m/e 226.93 (M^+ ; calc. 227.01). (Found: C, 50.3; H, 4.75; N, 5.4; Cl, 14.5. Calc. for $\text{C}_{32}\text{H}_{36}\text{Cl}_3\text{N}_3\text{O}_{12}$: C, 50.5; H, 4.8; N, 5.5; Cl, 14.0%.)

18-Crown-6- $\text{Bu}^+\text{NH}_3(\text{NC})_2\text{C}=\text{C}(\text{CN})\text{O}$. The 18-crown-6- $\text{Bu}^+\text{NH}_3(\text{NC})_2\text{C}=\text{C}(\text{CN})\text{O}$ complex was obtained by equilibration of 2 ml of an aqueous solution of tricyanoethanol¹⁴ (2 mmol ml^{-1}) and $\text{Bu}^+\text{NH}_3\text{Cl}$ (2 mmol ml^{-1}) with 4 ml of a chloroform solution of 18-crown-6 (1 mmol ml^{-1}). After separation of the two layers and drying of the organic layer diethyl ether was added. The 18-crown-6- $\text{Bu}^+\text{NH}_3(\text{NC})_2\text{C}=\text{C}(\text{CN})\text{O}$ precipitated from the solution (82%), m.p. 104–105 °C; $\delta(\text{CDCl}_3)$ 3.70 (s, 24 H, OCH_2) and 1.42 (s, 9 H, CH_3) (Found: C, 55.1; H, 7.9; N, 12.1. Calc. for $\text{C}_{21}\text{H}_{36}\text{N}_4\text{O}_7$: C, 55.2; H, 7.9; N, 12.3%).

X-Ray Diffraction.—X-Ray diffraction measurements were performed on a single-crystal diffractometer (Philips PW 1100) using graphite-monochromated $\text{Cu-K}\alpha$ radiation at 145 K, ω -2 θ scan mode, scan speed (ω) 0.05° s^{-1} , $3 < \theta < 60$, scan width (ω) (1.8 + 0.5 $\text{tg}\theta$)°, number of reflections measured: 5 246, number of reflections with $I > \sigma(I)$: 3 956; the latter reflections have been used in the structure solution and refinement. Crystal data: $\text{C}_{32}\text{H}_{36}\text{Cl}_3\text{N}_3\text{O}_{12}$, orthorhombic, space group $Pbca$, $a =$

31.66(2), $b = 15.546(3)$, $c = 14.358(5)$ Å, $Z = 8$. The structure was refined by block-diagonal least squares to a final R factor of 8.9%. Number of parameters in last cycle: 548. Hydrogen atoms of the crown ether were found from difference synthesis; hydrogen atoms of the *t*-butylammonium ion could not be found due to large thermal motion.

Interactions of Crown Ethers, Halide Salts, and TCNE.—*Dibenzo-18-crown-6*, $\text{Bu}^1\text{NH}_3\text{Br}$ or KBr , and *TCNE*. $\text{Bu}^1\text{NH}_3\text{Br}$ or KBr^* (0.5 mmol ml^{-1}) was added to a chloroform solution containing *dibenzo-18-crown-6* (0.5 mmol ml^{-1}) and *TCNE* (0.5 mmol ml^{-1}). The colour of the solution immediately changed from blue to red with λ_{max} 540 nm.

18-Crown-6, $\text{Bu}^1\text{NH}_3\text{Br}$ or KBr , and *TCNE*. $\text{Bu}^1\text{NH}_3\text{Br}$ or KBr^* (0.5 mmol ml^{-1}) was added to a chloroform solution containing *18-crown-6* (0.5 mmol ml^{-1}) and *TCNE* (0.5 mmol ml^{-1}). The colour of the solution immediately changed from light yellow to red with λ_{max} 450 nm.

Dibenzo-18-crown-6, $\text{Bu}^1\text{NH}_3\text{Cl}$ or KCl , and *TCNE*. $\text{Bu}^1\text{NH}_3\text{Cl}$ or KCl^* (0.5 mmol ml^{-1}) was added to a chloroform solution containing *dibenzo-18-crown-6* (0.5 mmol ml^{-1}) and *TCNE* (0.5 mmol ml^{-1}). The colour of the solution changed gradually from blue to green. This green colour was shown to be a combination of blue and yellow with absorptions at 400 and 590 nm. The absorption at 590 nm could be attributed to the charge-transfer complex of *dibenzo-18-crown-6* and *TCNE*. The absorption at 400 nm could be attributed to the charge-transfer complex of *TCNE* with the halide anion, as was proven by the interaction of *18-crown-6*, $\text{Bu}^1\text{NH}_3\text{Cl}$ or KCl , and *TCNE*.

18-Crown-6, $\text{Bu}^1\text{NH}_3\text{Cl}$ or KCl , and *TCNE*. $\text{Bu}^1\text{NH}_3\text{Cl}$ or KCl^* (0.5 mmol ml^{-1}) was added to a chloroform solution containing *18-crown-6* (0.5 mmol ml^{-1}) and *TCNE* (0.5 mmol ml^{-1}). The colour of the solution immediately changed from light yellow to deep yellow with λ_{max} 400 nm.

18-Crown-6, KF , and *TCNE*. KF^* (0.5 mmol ml^{-1}) was added to a chloroform solution containing *18-crown-6* (0.5 mmol ml^{-1}) and *TCNE* (0.5 mmol ml^{-1}). The colour of the solution immediately changed from light yellow to red with λ_{max} 400 nm.

Solutions of all the above complexes in CHCl_3 showed strong e.s.r. signals corresponding to the spectrum of the $\text{TCNE}^{\cdot-}$ radical anion.

Determination of the Association Constant.—For a series of CHCl_3 solutions, containing (7) or (8) and *TCNE* with various concentrations of both the crown ether and *TCNE*, the extinction was measured in a 1 ml cuvette with a pathway of 1 cm [$l = 1$; equation (2)]. The concentrations were varied in such a way that the observed extinction varied from 0.2–0.8. K, ϵ combinations were chosen until a minimum was found for the function F (equation (3)). F is a minimum if $\partial F/\partial \epsilon = 0$ or $\epsilon = \sum_i (E_i \cdot [\text{AD}]_i) / \sum_i [\text{AD}]_i^2$. Therefore, F has only to be minimized for K . For a chosen K value, $[\text{AD}]_i$ is calculated from

equation (4). As a first approximation the K values evaluated from the Benesi–Hildebrand relationship¹⁸ (5) were used.

$$F(K, \epsilon) = \sum_i (E_i - \epsilon[\text{AD}]_i)^2 \quad (3)$$

$$[\text{AD}]_i = 1/2\{([\text{A}]_{0,i} + [\text{D}]_{0,i} + K^{-1}) - \sqrt{([\text{A}]_{0,i} + [\text{D}]_{0,i} + K^{-1})^2 - 4[\text{A}]_{0,i}[\text{D}]_{0,i}}\} \quad (4)$$

$$\frac{[\text{A}]_0}{E} = \frac{1}{K\epsilon} \cdot \frac{1}{[\text{D}]_0} + \frac{1}{\epsilon} \quad (5)$$

Acknowledgements

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* Added as a suspension of salt in chloroform.