Molecular Complexes of Crown Ethers. Part 2: Complexes between Crown Ethers and π Acceptors

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Abstract. The intermolecular charge transfer (CT) complexes of four crown ethers (CE), viz. B15C5, B18C6, DB18C6 and DB24C8 (as donors), and three acceptors, i.e. tetracyanoethylene (TCNE) 7,7,8,8-tetracyanoquinodimethane (TCNQ) and chloranil were studied in the UV-Visible region in 1,2-dichloroethane (DCE) at 298.2 K. Solid complexes were also prepared and the ratio of the donor to the acceptor was 1 : 1. Results indicate that the λ_{max} of the CT band decreases while K_c (formation equilibrium constant) increases following the systematic change of the electron affinity of the π acceptors. The K_c values suggest that the phenyl group in CE plays a major role in the formation of a CT complex.

Key words: Intermolecular charge transfer, crown ethers, π acceptors, formation constant, UV-visible spectra.

1. Introduction

Since their synthesis by Pedersen [1], crown ethers (CE) have received ever increasing attention [2–4] as an extractant for alkali and alkaline earth metals. Most effort has been concentrated on the ionic complexes of crown ethers, while little attention has been focused on the molecular complexes of CE with different acceptors [5–8]. In this communication we present some results concerning the complex formation between four CEs (B15C5, B18C6, DB18C6 and DB24C8) and three acceptors (TCNE, TCNQ and chloranil) in DCE and compare K_c values obtained in this study with those obtained previously by others [6, 7] using DCM as solvent.

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2. Experimental

All UV-visible spectral measurements were obtained with a Shimadzu spectropho-
tometer (UV-160), using 1 cm fused silica cells. Donor concentrations were kept
within 1.2×10^{-1}–1×10^{-2} M while the acceptor concentration was kept constant
at 1×10^{-3} M. IR spectra were recorded using KBr discs. All solvents (BDH)
were of spectroscopic grade and were dried over molecular sieve. CEs were of
pure grade (Fluka). TCNE (Aldrich) was recrystallized twice from chlorobenzene
and then sublimed, TCNQ (Aldrich) was recrystallized twice from benzene. DCE
was used in this study due to its availability and its physical properties are similar
to DCM.

A. PREPARATION OF SOLID COMPLEXES

The acceptor (0.2 mmol) in 5 mL DCE was added to a solution of 0.2 mmol of
the CE in 5 mL DCE. The solution was allowed to evaporate slowly at room
temperature and the solid formed was recrystallized from DCE and its physical
properties were determined (Table I).

B. CALCULATIONS

Calculation of the equilibrium constant for complex formation, K_c, and molar
absorbtivity, ϵ_c, were based on the Benesi–Hilderbrand equation [10]:

$$[A_0]/A = 1/(K_c \times \epsilon_c) \times 1/[D_0] + 1/\epsilon_c. \tag{1}$$

Where A is the absorbance due to complex formation. $[A_0]$ and $[D_0]$ are the initial
concentrations of the acceptor and the donor, respectively. The ionization potential,
IP, values of CEs have been calculated using the following equation [10].

$$h\upsilon = a\text{IP} + b. \tag{2}$$

a and b are constants, with $a = 0.92$ and $b = -5.12$.

3. Results and Discussion

Table I gives the physical properties of the solid 1 : 1 CE acceptor complexes.

The IR absorptions of a representative complex are given in Table II. As a general
trend the CN group shows a small shift to lower frequency on complexation. This
shift is indicative of higher charge density on the CN group of the acceptor. The
3000–2800 cm^{-1} region is assigned to the methylene stretching of the ethoxy group
coupled with a ring vibration, shifted to a lower frequency (2980–2899 cm^{-1}) in
the presence of the acceptor. This effect can be ascribed to the participation of the
ethoxy oxygen electron in the charge transfer interaction with the acceptor. This is

TABLE I. Some experimental and physical properties of CE complexes.

Complex	Formula	M.p. (°C)	Color	C%	H%	N%
B15C5–TCNE	$C_{20}H_{20}N_4O_5$	57–58	dark blue	(60.25)	(5.05)	(14.56)
				60.54	5.09	14.13
B18C6–TCNE	$C_{22}H_{24}N_4O_6$	**	dark blue	55.99	5.49	12.71
DB18C6–TCNE	$C_{26}H_{24}N_4O_6$	143–145	dark blue	(63.66)	(4.86)	(11.36)
				63.93	4.95	11.47
DB24C8–TCNE	$C_{30}H_{32}N_4O_8$	158–159	pale yellow	(62.0)	(5.08)	(9.65)
				62.49	5.59	9.73
B15C5–TCNQ	$C_{26}H_{24}N_4O_5$	65–66	olive green	(65.98)	(5.03)	(11.67)
				66.09	5.12	11.85
B18C6–TCNQ	$C_{28}H_{28}N_4O_6$	44–47	brown*	–	–	–
				65.12	5.64	10.84
DB18C6–TCNQ	$C_{32}H_{28}N_4O_6$	123–126	pale yellow	(70.0)	(4.66)	(9.61)
				68.08	4.99	9.92
DB24C8–TCNQ	$C_{36}H_{36}N_4O_8$	96–98	pale brown	(67.01)	(5.55)	(8.9)
				66.25	5.56	8.58
B15C5–Chloranil	$C_{20}H_{20}C_{14}O_7$	49–51	green yellow	(46.03)	(3.81)	
				46.71	3.92	
B18C6–Chloranil	$C_{22}H_{24}C_{14}O_8$	**	yellow	–	–	
				47.32	4.33	
DB18C6–Chloranil	$C_{26}H_{24}C_{14}O_8$	112–113	pale green	(50.98)	(3.9)	
				51.49	3.99	
DB24C8–Chloranil	$C_{30}H_{32}C_{14}O_{10}$	97–98	pale green	(51.6)	(4.58)	
				51.88	4.64	

( ) Experimental.
*Elemental analysis was not done because of the failure to obtain crystals.
**Semi-solid.

TABLE II. Infrared spectral data of the CE–TCNE complexes (v in cm^{-1}).

Compound	$v(CH_2)$	$v(CN)$
TCNE	–	2265, 2220, 2210
B15C5	3000–2810	–
B15C5–TCNE	2980–2800	2260, 2200
DB18C6	2985–2810	–
DB18C6–TCNE	2955–2804	2265, 2210, 2200
DB24C8	2960–2815	–
DB24C8–TCNE	2924–2805	2250, 2210, 2194

an indication of a charge migration from the CE to the acceptor, resulting in lower charge density on the ethoxy group.

A study of the possible formation of CT complexes between CEs and the three acceptors showed that only benzo-substituted CEs give evidence of such an interaction. Thus a new band in the visible region of the spectrum appeared after mixing solutions of CEs with the acceptors in DCE, and a shoulder also appeared on the long wavelength side of the acceptor absorption band. Figure 1 is a representative one, showing the CT band. Similar results were reported in the case of CT complexes of TCNE with heterocyclic donors [11, 12] and were attributed to electron transitions from the donor molecules to the acceptor. The same interpretation may also be valid in the present case, thus the band at 580–592 nm may be assigned to a CT complex. A representative plot of the Benesi–Hildebrand equation, Figure 2, indicates that the ratio of the donor to the acceptor is 1 : 1. Table III shows the K_c values obtained for the four complexes together with values obtained by other workers [6, 7]. The K_c values are comparable, but the value obtained for the DB24C8–TCNE system in this work does not agree with that reported by Semnani $et\ al.$ [7]. For this system they reported λ_{max} to be 550 nm in DCM while in our system the value was 592 nm. The formation constant obtained for the four complexes cannot be explained completely as being due to CT from the aromatic ring of the CE to the acceptor, since the reported K_c values for the similar aromatic systems benzene and xylene [11, 14] with the acceptor did not exceed 0.45. Charge transfer from the oxygen atoms of the CEs to the acceptor can also be eliminated because no such band appeared in the spectrum of 15C5 and 18C6 with the acceptor. Thus it may be concluded that the presence of a phenylene group is essential for the formation of the CT complex and demonstrates that complex formation is not due to the ether group but to the Ph—O—CH$_2$-structure.

For the present CT complexes one can draw the following conclusions: the complexes formed are sensitive to the basicity of the ethers, and the electron affinity of the acceptors. The following trend was obtained for the decrease in λ_{max} with decrease of the electron affinity of the acceptor.

TCNE > TCNQ > Chloranil.

K_c values increase in the same direction. The reader may note that, besides the expected influence of the basicity of the CEs, there are additional factors contributing to the value of K_c, such as the conformational flexibility of the CE. It is reported that DB18C6 has a rigid structure compared with other crown ethers [14, 15]. This conformation enables the acceptor to approach the plane of the benzo ring in DB18C6. On the other hand, B18C6 and B15C5 have one benzo group, which makes them more flexible and less geometrically suitable for the interaction with the acceptor. For DB24C8 it has been reported [7] that this ether is flexible and it adopts a geometry suitable for intermolecular interaction between the two benzo groups and this will decrease its interaction with the acceptor. In our case
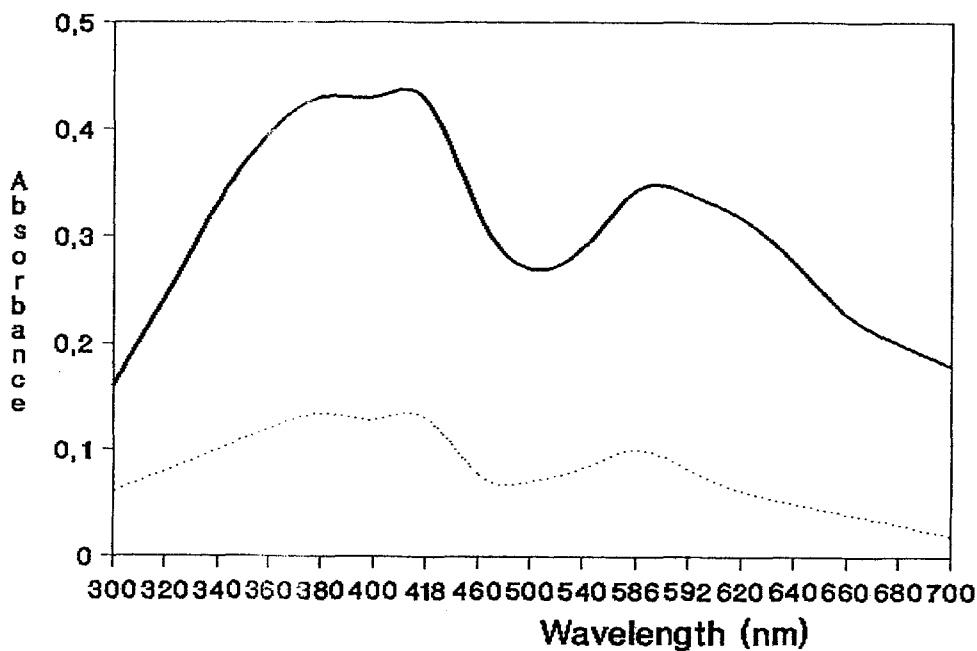
Fig. 1.   Absorption spectra of 1,2-dichloroethane solution of TCNE (1.352×10^{-3} M) at 25 °C with 0.026 (- - - - -) and 0.1846 M (—) of DB18C6.
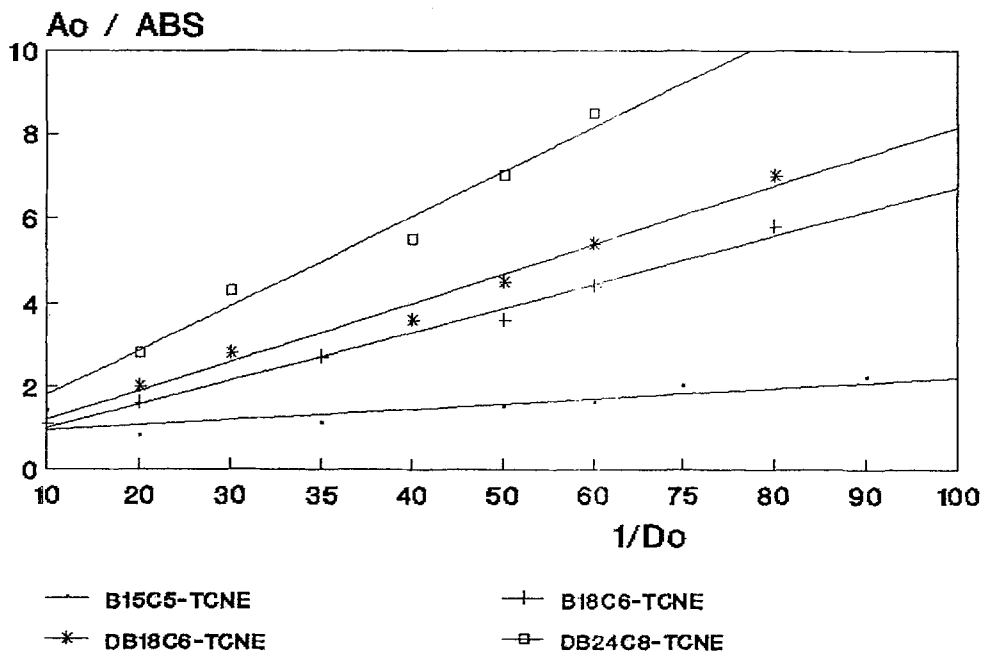

Fig. 2.   Typical Benesi–Hildebrand plots for different crown ethers with TCNE in DCE.

TABLE III. Maximum absorption wavelength λ_{max} (nm), molar absorbtivity ϵ_c (mol^{-1} cm^{-1} L), formation constant K_c (dm^3 mol^{-1}), product of ϵK_c (L^2 mol^{-2} cm^{-1}), free energies $-\Delta G^*$ (kJ mol^{-1}) and ionization potentials IP (eV) of the complexes in DCE.

Complex	λ_{max}	$K_c{}^{**}$	ϵ_c	$\epsilon.K_c$	$-\Delta G^*$	IP
B15C5–TCNE	580	2.3	166 ± 10	388	2.06	7.89
	419	(2.3)^a				
B18C6–TCNE	583	2.7	222 ± 12	609	2.46	7.87
	417					
DB18C6–TCNE	586	3.9	250 ± 15	965	3.37	7.86
	418	(3.4)^a				
DB24C8–TCNE	592	7.5	116 ± 9	870	4.99	7.84
	420	(2.7)^a				
B15C5–TCNQ	569	1.6	365 ± 18	581	1.17	7.93
B18C6–TCNQ	570	2.0	386 ± 18	776	1.72	7.93
DB18C6–TCNQ	570	3.7	437 ± 20	1627	3.24	7.93
DB24C8–TCNQ	572	5.3	443 ± 19	2347	4.13	7.92
B15C5–Chlor*	500	1.0	235 ± 18	246	0.24	8.73
B18C6–Chlor*	518	2.1	213 ± 16	453	1.84	89.64
DB18C6–Chlor*	526	3.6	242 ± 16	869	3.18	8.57
DB24C8–Chlor*	531	4.3	307 ± 20	1315	3.62	8.54

*Chloranil.
**Correlation is 0.998 and 0.996, errors in K_c range from 0.19 to 0.24.
^{a}Values obtained in DCM [6, 7].

K_c for DB24C8 is higher than that for DB18C6, which rules out such a geometry for our complex.

References

1. C.J. Pedersen:, *J. Am. Chem. Soc.* **89**, 707 (1967).
2. J.D. Lamb, R.M. Izatt, J.J. Christensen, and D.J. Eatough: *Coordination Chemistry of Macrocyclic Compounds* (Edited by G.A. Melson), Plenum Press, New York (1979).
3. G.W. Gokel and S.H. Korzeniowski: *Macrocyclic Polyether Synthesis*, Springer-Verlag, Berlin (1982).
4. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
5. H.P. Hopkins, D.V. Jahagirdar, and J.J. Windler: *J. Phys. Chem.* **82**, 1254 (1978).
6. A.M. Nour El-Din: *Spectrochim. Acta* **42A**, 637 (1986).
7. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
8. S.R. Salman and S.M. Al-Marsoumi: *Spectrochim. Acta* **49A**, 435 (1993).
9. H.A. Benesi and J.H. Hildebrand: *J. Am. Chem. Soc.* **71**, 2703 (1949).
10. R. Foster: *Organic Charge Transfer Complexes*, Academic Press (1969).
11. G. Aloise, S. Santini, and S. Sorrise: *J. Chem. Soc. Faraday Trans. 1.* **70**, 1908 (1974).
12. A. Cipicani, S. Santini, and G. Savelli: *J. Chem. Soc. Faraday Trans. 1* **75**, 497 (1979)
13. J.E. Frey, A. Andrew, D. Anokoviac, D.N. Beaman, L. Dupont, T. Elsner, S. Lang, M.O. Zwarto, R. Seagle, and C. Torreano: *J. Org. Chem.* **55**, 606 (1990).

14. S. Kashanian and M. Shamsipur: *Anal. Chim. Acta* **155**, 203 (1989).
15. M.K. Amini and M. Shamsipur: *J. Solution Chem.* **21**, 275 (1992).