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Molecular Complexes of Crown Ethers. Part 3. Effect of Cations on Charge Transfer Complexes with TCNE

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Abstract. The intermolecular charge transfer complexes (CT) of two crown ethers (CE), viz, B15C5 and DB18C6 (as donors), and tetracyanoethylene (TCNE), as acceptor, were studied in the UV-visible region in dichloroethane (DCE), at 298.2 K. The sequence of addition of the cation was varied in the case of B15C5 such that in one system the sequence was (CE + Cation) + TCNE and in the other (CE + TCNE) + cation. These two systems were found to be non-interchangeable, even under reflux conditions, giving different K_c values which were explained as being due to the different geometries of the CE. For the first sequence, the values most affected depended on the fit of the metal cation with the ether cavity, thus in B15C5, Na^+ showed the greatest effect, while for DB18C6 it was K^+.

Key words: Crown ethers, tetracyanoethylene, UV-visible spectroscopy, formation constant, effect of cations on formation constant.

1. Introduction

Complexes between crown ethers (CE) and different acceptors are receiving increasing attention [1–5]. CEs are considered to be a selective extractant for many cations [6–8]. It was found that during their complexation with alkali metal cations, CEs undergo geometrical changes which might affect the formation of these complexes. Little is known about the effect of the presence of metal ions on the complexes between crown ethers and π acceptors. In a previous paper [5] it was found that TCNE interacts with benzo-substituted CEs, and not with unsubstituted CEs, which suggests that the interaction between B15C5 and DB18C6 and TCNE is due to the participation of the Φ—OCH2CH2 moiety. This paper is concerned with the effect of cation addition on the formation constant between CE and TCNE.

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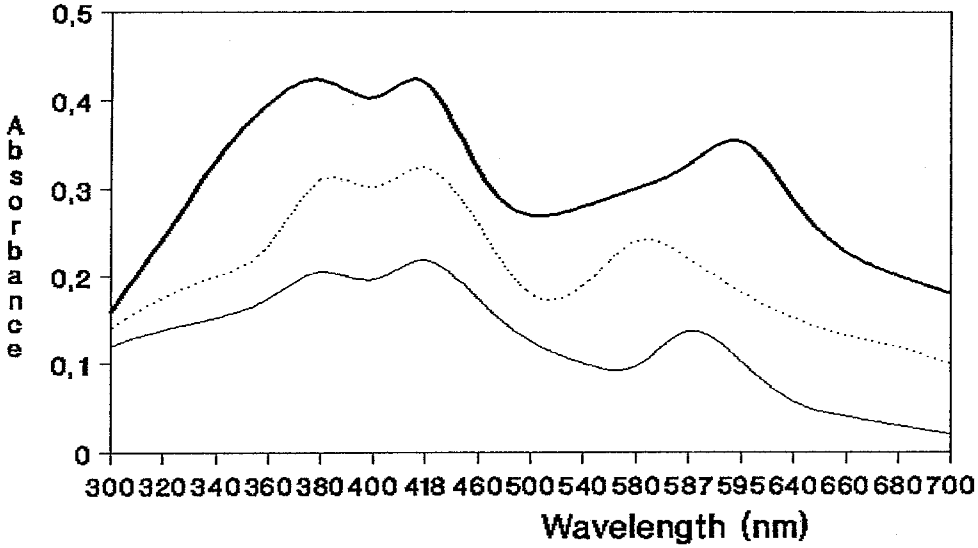

Fig. 1. Absorption spectra of 1,2-dichloroethane solution of: .... (B15C5 + TCNE); —— (B15C5 + TCNE) + Na; —— (B15C5 + Na) + TCNE.

2. Experimental

All UV-visible spectral measurements were carried out at 25 ± 1 °C in a Shimadzu spectrophotometer (UV-160) using 1 cm fused silica cells. Donor concentrations were kept within the range 1.2×10^{-1}–$\times 10^{-2}$ M, while the acceptor concentration was kept constant at 1×10^{-3} M. Dichloroethane (BDH) was of spectroscopic grade and was dried over molecular sieve. B15C5 and DB18C6 were pure grade (Fluka). Tetracyanoethylene, TCNE (Aldrich), was recrystallized twice from chlorobenzene and then sublimed.

Calculation of the formation constant K_c and molar absorptivity ε_c were performed using the Benesi–Hilderbrand equation [9]

$$[A_0]/A = 1/(K_c\varepsilon_c) \times 1/[D_0] + 1/\varepsilon_c \qquad (1)$$

where A is the absorbance due to complex formation, $[A_0]$ and $[D_0]$ are the initial concentration of the acceptor and the donor, respectively. From this equation K_c and ε_c were calculated, the results indicating that the stoichiometry of the complex was 1 : 1. The effect of added salts was studied in two ways. In the first, a known concentration of the crown ether was prepared and the salt was added to the solution and after equilibrium was achieved TCNE was added (system A) and the spectrum of the solution was run. In the second method the CE and TCNE were mixed and the spectrum of the mixture was recorded after the addition of the salt (system B). Representative spectra are shown in Figure 1.

TABLE I. Maximum absorption wavelength λ_{max} (nm), molar extinction coefficient ε (l mol^{-1} cm^{-1}) and formation constant K_c (dm^3 mol^{-1}) for B15C5 complexes.

Compound	λ_{max}	K_c**	ε	εK_c
B15C5 + TCNE	580	2.3 ± 0.07	116 ± 10	272 ± 25
B15C5 + Na + TCNE	587	35.3 ± 1.5	50 ± 5	1783 ± 18
B15C5 + K + TCNE	582	20.4 ± 1.1	103 ± 10	2104 ± 20
B15C5 + TCNE + Na	595	5.6 ± 0.5	306 ± 30	1698 ± 17
B15C5 + TCNE + K	580	13.6 ± 1.3(3.66)*	69 ± 6	942 ± 30

*Ref. 2.
**Correlation is 0.998 and 0.996, errors in K_c range from 0.18 to 0.24.

TABLE II. Maximum absorption wavelength (λ_{max}), molar extinction coefficient ε (l mol^{-1} cm^{-1}) and formation constant (dm^3 mol^{-1}) for DB18C6 complexes.

Compound	λ	K_c**	ε	εK_c
DB18C6 + TCNE	586	3.86 ± 0.15(3.97)*(3.39)+	250 ± 15	965 ± 30
DB18C6 + Na + TCNE	582	6.3 ± 0.18	263 ± 70	1656 ± 40
DB18C6 + K + TCNE	577	9.2 ± 0.6(1.84)*(6.41)+	302 ± 25	2058 ± 60

*Ref. 2 and Ref 3.
**Correlation is 0.999 and 0.998, error in K_c range from 0.15 to 0.25.

3. Results and Discussion

The calculated K_c for the B15C5–TCNE and DB18C6–TCNE complexes in the presence and absence of the cation are given in Tables I and II. Two mechanisms for complex formation can be suggested:

Mechanism A

$$\mathrm{CE} + \mathrm{M}^+ \rightleftharpoons \mathrm{CE{\cdot}M}^+$$

$$\mathrm{CE{\cdot}M}^+ + \mathrm{A} \rightleftharpoons (\mathrm{CE{\cdot}M})^+\text{—A}$$

Mechanism B

$$\mathrm{CE} + \mathrm{A} \rightleftharpoons \mathrm{CE{\cdot}A}$$

$$\mathrm{CE{\cdot}A} + \mathrm{M}^+ \rightleftharpoons (\mathrm{CE{\cdot}A})\text{—}\mathrm{M}^+$$

If the final complex is the same for the two systems then they must give very similar values for K_c and ε. To examine this, two solution systems were prepared, the first solution was $\{(\mathrm{CE} + \mathrm{M}^+) + \mathrm{TCNE}\}$ and the second was $\{(\mathrm{CE} + \mathrm{TCNE}) + \mathrm{M}^+\}$.

The two solutions were left for one day and then they were refluxed and their UV spectra measured.

No change was observed for the spectrum of each solution relative to the original solution before reflux, indicating that the two systems are independent and the resulting complexes are not interchangeable. Table I shows that when sodium salt was added to the {B15C5–TCNE} complex to produce system B, viz., {(B15C5–TCNE)Na^+}, there followed a marked shift in the charge transfer band from 580 nm to 595 nm together with a sharp increase in the $(\varepsilon.K_c)$ value from 272 to 1698 giving for K_c a value more than twice that for the complex in the absence of the cation, as well as a marked increase in the absorptivity value.

Interestingly, for the system {(B15C5 + Na^+) + TCNE}, while having a slightly greater value for $(\varepsilon.K_c)$ (1783 compared with 1698), the shift in λ_{max} of the CT band was half as much as that for system B. However, K_c showed a much greater change in this system, about 35 as compared to 5.6 for system B, while the value for ε showed an opposite trend, changing from 306 in system B to only 56 in system A.

Tables I and II show that K_c behaves in accordance with the specificity of the ether toward the alkali metal cation, giving the highest K_c value with sodium ion in the case of B15C5, and with potassium ion in the case of DB18C6. For λ_{max}, the observed shifts of the CT bands in the presence of the cations, as compared with those in their absence, are in opposite directions for the two CT complexes. However the shift, whether red or blue, again follows the ether specificity toward the cations. Thus $\Delta\lambda$ for K^+ in DB18C6 was the greatest with a blue shift of 9 nm, while Na^+ in B15C5 had the greatest red shift of 7 nm. It seems that the effect of the metal cation on the donicity of the ether towards the acceptor TCNE is different in B15C5 and in DB18C6. Thus the latter, with a marked red shift, indicates that (B15C5 + M^+) is a softer donor than free B15C5, while for DB18C6 where the opposite effect is observed indicating that (DB18C6 + M^+) is harder than the free ether. This may be due to the effect of the metal cation on the electron density of the symmetrically substituted donor ether, DB18C6, which is greater and different than the less symmetric B15C5. With the latter the asymmetry of (B15C5 + M^+) may cause back donation from the acceptor TCNE to the metal–ether complex thus enhancing its softness. Although TCNE has high electron affinity, it is difficult to back donate electrons, but this may be possible in the presence of the cation. This may explain our results. As for DB18C6, this CE is selective for potassium ion, which fits into the cavity of the crown, forming a stable complex, with the metal bound very tightly to the unshared pair of the electrons on the oxygen atoms [10, 14]. It is known that DB18C6 has the most rigid structure [15, 16], therefore TCNE can approach it and interact with it in a planar conformation. The ion interacts with this complex and will stabilise it thus the K_c value increases.

The K_c value for B15C5 complexes increased sharply when the crown ether is mixed first with the salt and then TCNE is added. It is believed that sodium causes B15C5 to flatten [10], thus increasing the interaction with TCNE. The cavity radius of B15C5 is 85–110 pm [11], that of sodium is 102 pm [12] and that of potassium is 138 pm [12]. The cavity diameter of B15C5 increases from 120 to 172 and 184 pm upon the addition of Na^+ and K^+, respectively [13]. It seems that sodium fits nicely into the B15C5 cavity and that explains why we obtained large values of K_c when NaCl was added, followed by TCNE. Although there is evidence for the formation of a 2 : 1 adduct between B15C5 and Na^+ [18–20], one is reluctant to suggest that in the case of (B15C5 + Na^+) + TCNE a 1 : 1 complex is formed and this may explain the large value obtained for K_c (about 35). The B15C5 cavity, on the other hand, is small compared to a K^+ ion thus a 2 : 1 adduct may be formed [17], thus reducing the extent of interaction with TCNE. The above assumption for the two systems may be supported by the difference in K_c obtained for the two systems while, if we assume that the complex between B15C5 and sodium is 2 : 1, then one would expect nearly similar values for K_c for the sodium and potassium systems, which is not the case.

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References

1. H.P. Hopkins, D.V. Jahagirdar and J.J. Windler: *J. Phys. Chem.* **82**, 1254 (1978).
2. A.M. Nour El-Din, *Spectrochim. Acta* **42A**, 637 (1986).
3. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
4. S.R. Salman and S.M. Al-Marsoumi, *Spectrochim. Acta* **49A**, 435 (1993).
5. G.A.W. Derwish, S.R. Salman and M. Al-Marsoumi: *J. Incl. Phenom.* **20**, 123–129 (1995).
6. J.D. Lamb, R.M. Izatt, J.J. Christensen and D.J. Eatough: *Coordination Chemistry Of Macrocyclic Compounds* (G. A. Melson, ed.), Plenum Press, New York (1979).
7. G.W. Gokel and S.H. Korzeniowski: *Macrocyclic Polyethers Synthesis*, Springer-Verlag, Berlin (1982).
8. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen: *Chem. Rev.* **85**, 271 (1985).
9. H.A. Benesi and J.H. Hilderbrand: *J. Am. Chem. Soc.* **71**, 2703 (1949).
10. Y. Jayathirtha and V. Krishnan: *Indian. J. Chem.* **18A**, 311 (1979).
11. H.F. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
12. R.D. Shannon: *Acta. Crystallogr. Sect. A* **32**, 751 (1976).
13. G.A. Melson: *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York (1979).
14. G.W. Gokel and H.D. Durst: *Aldrichim. Acta* **9**, 1 (1976).
15. S. Kashanian and M. Shamsipur: *Anal. Chim. Acta* **155**, 203 (1989).
16. M.K. Amini and M. Shamsipur: *J. Solution. Chem.* **21**, 275 (1992). M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).
17. R.M. Izatt, R.E. Terry, D.P. Nelson, Y. Chan, D.J. Eatough, J.S. Bradshaw, L.D. Hansen and J.J. Christensen: *J. Am. Chem. Soc.* **98**, 7626 (1976).
18. G. Michaux and J. Reisse: *J. Am. Chem. Soc.* **104**, 6895 (1982).
19. T. Miyazaki, S. Yanagida, A. Itoh and M. Okahara: *Bull. Chem. Soc. Jpn.* **55**, 2005 (1982).
20. J.D. Lin and A.I. Popov: *J. Am. Chem. Soc.* **103**, 3773 (1981).