

Molecular Complexes of Crown Ethers, Part 4: Complexes of Crown Ethers with Picric Acid

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Abstract. The intermolecular charge-transfer spectra of seven crown ethers (CE), viz, 15C5, 18C6, B15C5, B18C6, DC18C6, and DB24C8, with picric acid (PA) were studied in the UV-visible region in 1,2-dichloroethane (DCE) at 298.2 K. The complex formation equilibrium constant values, K_c , suggest that many factors contribute to K_c , among them crown ether conformation, size and the presence of an aromatic ring in the CE.

Key words: UV-visible spectroscopy, donor–acceptor charge transfer band, crown ethers, 15C5, 18C6, B15C5, B18C6 and DB24C8, picric acid, effect of salt on charge transfer band, conformation of crown ether.

1. Introduction

Molecular complexes of crown ethers with acceptors in which charge-transfer may take place are receiving increasing attention [1–4]. It is known that the importance of crown ethers in solvent extraction and complex formation with metals is due to their selectivity [5–8].

The formation of crown ether complexes with metal cations may be affected by many factors. These factors can be tested when the effect of metal cations on the charge-transfer complexes between crown ethers and some electron acceptors are studied in the presence, for example, of alkali metal salt. This may be done by studying the effect such metal cations have on the formation constants of the crown ether complexes with some acceptors [1, 2, 4]. It is known that picric acid is used to enhance the extraction and complex formation of metal cations with CEs. Picric acid is also known to form a wide range of CT complexes [9] with a variety of donors, but only the complex of PA with B15C5 has been reported [10].

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In this communication we present some data concerning the complex formation of seven CEs (viz. 15C5, 18C6, B15C5, B18C6, DC18C6 and DB24C8) with picric acid, and the effect of adding cations on the formation constant of these complexes.

2. Experimental

Infrared spectra were recorded on a Pye-Unicam SP3-300 double beam IR spectrophotometer, using KBr discs. $^1\text{H-NMR}$ spectra were run on a Jeol JNM EX-90 FT NMR machine operating at 90 MHz for protons. CD_2Cl_2 was used as solvent with TMS as an internal reference. Sweep width was 1 KHz, flip angle 45° , acquisition time 2 s. All UV-visible spectra measurements were carried out on a Shimadzu spectrophotometer (UV160), using 1 cm fused silica cells. The donor concentration was varied within the range 1.2×10^{-1} – 1.0×10^{-2} M while the acceptor concentration was kept constant at 1×10^{-3} M. The effect of salt was studied by adding solid salt to the CE solution, the acceptor was added after 5 minutes and the measurements were carried out. Dichloroethane (BDH) was of spectroscopic grade and was dried over molecular sieve. Crown ethers were of pure grade (Fluka) and used without further purification. Picric acid (Aldrich) was of pure grade and was used without treatment but was kept dry using P_2O_5 . In order to check the water content of PA its IR spectrum was run using KBr discs. The spectrum did not show a band corresponding to water absorption, but it showed an intramolecular H-bonded hydroxy absorption belonging to PA. Attempts have been made to obtain solid complexes by mixing equimolar amounts of picric acid with different donors. Isolation of 18C6, B15C5 and DB18C6-picric acid solid complexes were quite successful but not in the case of 15C5, B18C6 and DC18C6 where semi-solid products were obtained, which made it difficult to run their elemental analysis. Table I gives some physical properties and elemental analysis results of CE-picric acid complexes.

3. Results and Discussion

Two bands in the visible region at (375–380 nm) and (413–440 nm) (the last band appeared as shoulder), were observed after mixing solutions of CEs 15C5, 18C6 and DC18C6 with picric acid in 1,2-dichloroethane, DCE (Figure 1). These two bands were assigned to CT bands due to complex formation. CEs and picric acid did not show any absorption in this region when they were taken separately. Picric acid solution in DCE shows two absorptions, at 256 nm ($\epsilon = 29797$) and at 338 nm ($\epsilon = 5143$). In order to record the CT spectrum we used the spectral subtraction method by using the same concentration of PA in the sample and reference cells. The Benesi–Hildebrand equation [11] was applied to evaluate ϵ and K_c of the CT complexes [4]. Typical plots are shown in Figure 2. They all gave good correlation coefficients. Table II gives the absorption maxima λ_{max} of the CT complexes, their molar extinction coefficients and the formation constants K_c . From these results,

Table I. Physical properties and C, H, N analysis of CE-PA complexes.

Complex	M. Formula. M.Wt	M.pt °C	Color	%C ([*])	%H ([*])	%N ([*])	%O
15C5-PA	C ₁₆ H ₂₃ N ₃ O ₁₂ 449.36	**	Pale yellow	42.77	5.16	9.35	42.73
18C6-PA	C ₁₈ H ₂₇ N ₃ O ₁₃ 493.43	46-48	Yellow	43.82 (43.46)	5.52 (5.29)	8.51 (7.99)	42.15
B15C5-PA	C ₂₀ H ₂₃ N ₃ O ₁₂ 497.42	51-53	Yellow	48.29 (48.18)	4.66 (4.62)	8.44 (8.21)	38.59
B18C6-PA	C ₂₂ H ₂₇ N ₃ O ₁₃ 547.46	**	Greenish- yellow	48.27	4.97	8.77	37.99
DB18C6-PA	C ₂₆ H ₂₇ N ₃ O ₁₃ 595.6	129.13	Orange	52.44 (52.18)	4.62 (4.56)	8.06 (7.83)	34.93
DC18C6-PA	C ₂₆ H ₃₉ N ₃ O ₁₃ 607.6	**	Yellow	51.39	6.47	7.89	34.2

(^{*}) Experimental.

** Semi-solid complex.

it is possible to suggest that for the alicyclic CEs 15C5, 18C6 and DC18C6 the K_c values increased with increasing ring size. With DC18C6, with the highest K_c , an explanation for this could be based on the presence of two cyclohexyl groups causing an increase in the basicity of the oxygen atoms in comparison with DB18C6, and to the ability of the DC18C6 complex to adapt to different conformations as required for greater stability of the complex.

Phenyl substituted CEs showed an enhanced K_c (compare B15C5 with 15C5 and B18C6 with 18C6). This might suggest that the aromatic group plays an important part in the donor ability of the ethers. The relative importance of the last two factors may be judged by the fact that the addition of another benzo group, as in DB18C6, caused the value of K_c to decrease due to the loss of flexibility of the ring. This supposition is supported by the fact that for DB24C8, the value of K_c is higher than for DB18C6, because of the larger ring size and greater flexibility.

Maria *et al.* [12] reported the IR spectra of molecular complexes of picric acid with compounds such as benzene, urea and pyridine. Perturbations in the vibrational spectra of donors and acceptors were observed. The type of electron donor-acceptor complexes were assigned as $n-\pi^*$ and $\pi-\pi^*$ and some evidence was found for the presence of hydrogen bonding (HB), which was also reported in other systems [13], where the frequency changes $\Delta\nu_{OH}$ caused by such bonding was reported to be between 2-10 cm^{-1} . The IR spectra of 18C6, B15C5, and DB18C6-picric acid complexes were determined in KBr pellets and compared with the parent materials. The comparison shows the following.

1. The intensity of the band at 3110 cm^{-1} , assigned to intramolecular HB [14] in picric acid had decreased. Other bands in the spectra of the CT complexes appeared

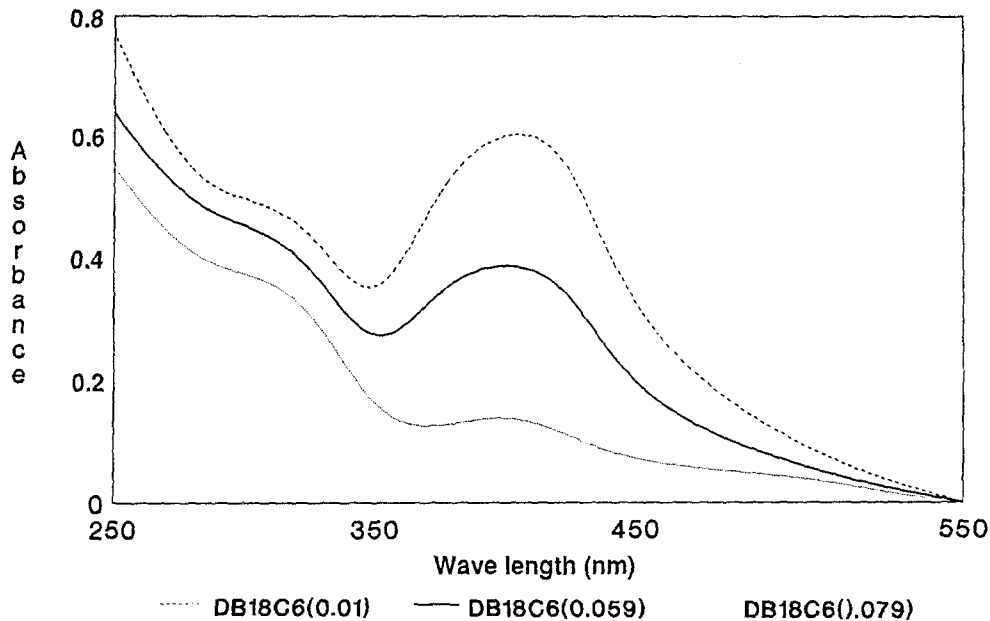


Figure 1. Absorption spectra of 1,2-DCE solution of picric acid (1.039×10^{-3} M) at 25 °C with different concentrations of DB18C6. ----- DB18C6(0.01 M); — DB18C6(0.059 M); DB18C6(0.079 M)

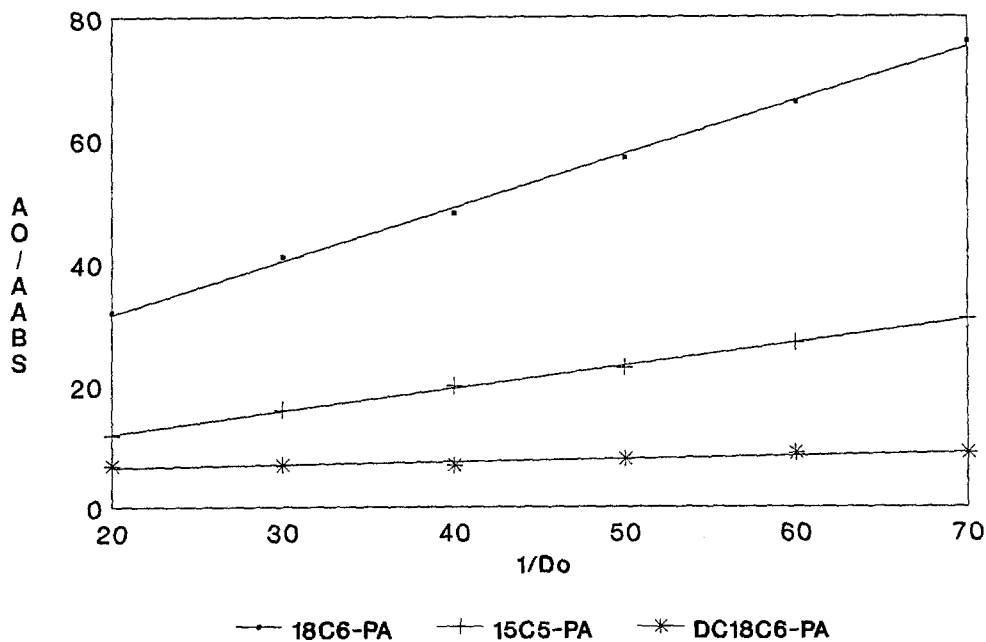


Figure 2. Typical Benesi-Hildebrand plots used in the calculation of K_c of complexes. —■— 18C6-PA; + 15C5-PA; —*— DC18C6-PA.

Table II. Maximum absorption wave length λ_{\max} (nm), molar extinction coefficient ϵ ($\text{mole}^{-1} \text{cm}^{-1}$), formation constant K_c ($\text{dm}^3 \text{mol}^{-1}$), product ϵK_c ($\text{l}^2 \text{mol}^{-2} \text{cm}^{-1}$) of the CT complexes formed between CE and PA in DCE at 298.2 K in the presence and absence of monovalent ions in 1,2-DCE at 298 K.

Compound	λ_{\max}	ϵ	K_c	$\epsilon \cdot K_c$
15C5 + PA	380	1146 ± 30	9.8 ± 0.4	11231
15C5 + NaCl + PA	376	585 ± 15	9.9 ± 0.6	5792
15C5 + KCl + PA	382	676 ± 17	13.2 ± 0.4	8923
18C6 + PA	379	304 ± 18	16.8 ± 0.7	5107
18C6 + NaCl + PA	388	920 ± 28	38.3 ± 0.3	35236
18C6 + KCl + PA	377	516 ± 16	20.6 ± 0.6	10630
B15C5 + PA	375	146 ± 15	34.1 ± 0.7	4979
B15C5 + NaCl + PA	369	223 ± 17	43.5 ± 0.8	9701
B15C5 + KCl + PA	381	780 ± 18	34.2 ± 0.6	26676
B18C6 + PA	377	101 ± 8	76.8 ± 1.0	7757
DB18C6 + PA	379	114 ± 9	20.5 ± 0.6	2337
DB18C6 + NaCl + PA	380	938 ± 28	11.7 ± 0.4	100975
DB18C6 + KCl + PA	374	595 ± 19	15.7 ± 0.5	10912
DC18C6 + PA	381	690 ± 20	188.7 ± 1.3	130203
DC18C6 + NaCl + PA	411	427 ± 16	144.9 ± 1.2	61872
DC18C6 + KCl + PA	381	523 ± 19	313.5 ± 1.2	163965
DB24C8 + PA	382	180 ± 11	37.4 ± 0.6	6732

Calculations based on the first absorption band since the 2nd band appeared only as a shoulder. Correlation coefficients of all readings are within 0.995–0.999.

as broad bands ($3580\text{--}3480 \text{ cm}^{-1}$) and are assigned to intermolecular HB, between CE and picric acid.

2. The $1430, 1350, 1270 \text{ cm}^{-1}$ peaks, assigned to the OH bending vibration in picric acid were shifted to lower wave number ($1420, 1340, 1244 \text{ cm}^{-1}$).

3. The 655 cm^{-1} band, assigned to OH out-of-plane vibration in PA, was shifted to lower wave number at 640 cm^{-1} .

The $^1\text{H-NMR}$ spectra of the DB18C6-PA complex was recorded in DCM, and compared with those of DB18C6 and PA separately. The comparison shows that the phenolic proton peak of picric acid at 11.8 ppm, which is related to intramolecular hydrogen bonding [14] between the phenolic proton and the adjacent nitro group, shifted to high field, appearing at 6.5 ppm in the DB18C6-PA complex, indicating the influence of complex formation on breaking the intramolecular HB in PA. This high-field shift of the hydroxy proton can be explained as being due to the conformation adapted by DB18C6 after complexation with the PA suggesting that the OH proton will be shielded by the ring current of the phenyl group of the DB18C6.

The effects of monovalent cations on the CE–PA complexes were investigated. To study the effect of monovalent cations on the formation and stability of the PA–CE complexes, the formation constant K_c was determined and their results are reported in Table II. From this table we notice the following trend in the order of decreasing K_c values:

1. For the free complex, i.e., CE + PA, and for Na^+ and K^+ ions the decreasing orders are:

Free: DC18C6 > B18C6 > B15C5 > DB18C6 > 18C6 > 15C5.

Na^+ ion: DC18C6 > B15C5 > 18C6 > DB18C6 > 15C5.

K^+ ion: DC18C6 > B15C5 > 18C6 > DB18C6 > 15C5.

2. When we examine the complexes formed for each CE we observe the following trend in decreasing K_c values:

DC18C6: K^+ > Free > Na^+

DB18C6: Free > K^+ > Na^+

18C6: Na^+ > K^+ > Free

B15C5: Na^+ > K^+ > Free

15C5: K^+ > Na^+ > Free

DC18C6 has five stereoisomers [15] and it is the most flexible and basic compared to the other four crown ethers. On the other hand DB18C6 has the most rigid structure among the crown ethers studied [16, 17]. B15C5 with only one benzo group, is more flexible than DB18C6, while 18C6 has four conformations. The open structure may accommodate large cations [18], the other conformations with higher polarity have six group-dipoles pointing toward the same side as found in 18C6–sodium complexes [19]. The order followed for the picric acid complexes is that of the order of basicity and donicity. Thus DC18C6 is the most basic and flexible to accommodate the requirement of interaction with the acid. Also 18C6 has more oxygen donor atoms than 15C5. In general the K^+ ion with an ionic radius of 1.38 Å [20] fits well inside the cavity of DB18C6 with a radius of 1.3–1.6 Å [21] so that the cation is bound tightly by the six oxygens [22]. With 15C5 and B15C5 the cavity is too small (0.85–1.1 Å [21]) to accommodate the K^+ ion and thus there is evidence that a 2 : 1 adduct is formed [23, 24]. Keeping these facts in mind, it is difficult to explain the data obtained in this work on the basis of ligand encapsulation of the cation only. Other factors may contribute [1–3]. It is believed that, except for DB18C6 which has a rigid structure, the presence of the cation

would flatten the crown ether thus enabling it to form a better CT with the acceptor picric acid. Thus one may expect that for Na^+ the highest K_c value would be with 15C5. For K^+ the highest value would be with DC18C6 and 18C6.

However, none of the above factors seem to dominate, but rather a combination of the following factors act synergically to produce the resultant effect. These factors are: configuration flexibility (flexibility for short), basicity, donicity, and cavity size. The CEs studied display these effects to varying extent, thus in DC18C6 we have the combination of flexibility, basicity and cavity size, and hence it appears as the CE with the highest value for all three sequences. This is followed by B15C5 which combines flexibility, donicity (through aromatic nucleus participation) and cavity size. This clearly fits the sequence for Na^+ , but for K^+ we must have the case of a 2 : 1 adduct to compensate the cavity size misfit.

For 18C6 we have the interesting case where we consider it together with DB18C6 in the PA series. Here the greater donicity of the latter makes its K_c value greater than that for 18C6. This effect (i.e., aromatic participation) seems to have priority over cavity size. Thus for K^+ we observe the sequence B15C5 > 18C6 although the latter gives the better cavity fit. Here the role of the PA in the formation of the complex may be evident. 15C5 occupies the end of all these series as it lacks flexibility, basicity and donicity relative to the other CEs. The role of PA in affecting the sequences which otherwise may be explained in terms of cavity size is evident when we compare the complexing trend of the free CEs to that of the CEs in the presence of PA. Thus for 18C6 and 15C5, which are specific for K^+ and Na^+ respectively, we observe that the order has been reversed. However when a benzo group is introduced which can act as a participant, possibly through charge-transfer to PA, the order of the free ethers is preserved.

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