



Crown Ether Complexes of Six-membered *N*-heteroaromatic Cations*

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Abstract

Crown ether complexes of six-membered *N*-heteroaromatic cations and the closely related bicyclic purinium cation (**6**) have been studied by ¹H NMR, mass spectrometric and crystallographic methods. The stability constants for the complexes were determined by ¹H NMR titration in acetonitrile solution and the complexation stoichiometry by ¹H NMR and ESI mass spectrometric methods. Altogether six crystal structures of complexes were determined to study the complexation in the solid state. Hydrogen bonding was observed to be the most important interaction for the complexation both in solution and in the solid state but π – π interactions also contribute to it. All crystal structures of the DB18C6 complexes with six-membered *N*-heteroaromatic cations, except for 4-hydroxypyridinium, are isomorphous to previously studied five-membered *N*-heteroaromatic cations and pyridinium complexes. Such a close resemblance is not observed in B18C6 and 18C6 complexes or DB18C6-purinium (**6**).

Introduction

Supramolecular chemistry has evolved from the efforts to mimic weak non-covalent interactions, such as hydrogen bonding, π – π and electrostatic interactions, of biological systems [1]. In biological systems many heterocyclic bases such as pyrimidine, imidazole and purine and especially their derivatives are of great importance due to their proton acceptor and hydrogen bonding abilities.

The ability of heterocyclic bases to form hydrogen bonded complexes has earlier been studied by Rebek *et al.*, who introduced a model receptor suitable for binding of for example heterocyclic diamines [2–4]. Several studies have also been performed to study the hydrogen bonding of heterocyclic bases with phenol derivatives [5–8].

In our previous studies we have investigated the complexation of tropylium [9, 10], pyridinium derivatives [11] and five-membered *N*-heteroaromatic cations [12, 13] with crown ethers. The tropylium cation forms a π -stacked complex with dibenzo-24-crown-8 (DB24C8, $K = 10 \text{ dm}^3 \text{ mol}^{-1}$) while the substituted amino- and hydroxytro-

pylium cations have also a possibility for hydrogen bonding ($K \sim 30 \text{ dm}^3 \text{ mol}^{-1}$ for both complexes). Crown ether complexes of pyridinium cation and its derivatives are stabilised by both hydrogen bonding and cation- π interactions. The main interaction between crown ethers and five-membered *N*-heteroaromatic cations is hydrogen bonding while cation- π interactions play only a secondary role.

In this work we report the complexation of pyrimidinium cation (**1**) with four different crown ethers. Additionally, we have studied the complexation of similar heterocyclic cations pyridazinium (**2**), pyrazinium (**3**), *N*-methylpyrimidinium (**4**), 4-hydroxypyridinium (**5**) and purinium (**6**) with dibenzo-18-crown-6 (DB18C6) (Scheme 1). The complexes were characterised by ¹H NMR, ESI MS (Electrospray Ionisation) and elemental analysis. We also report altogether six X-ray crystal structures of crown ether complexes; three pyrimidinium (**1**) complexes with different crown ethers and three DB18C6 complexes with pyridazinium (**2**), pyrazinium (**3**) and 4-hydroxypyridinium (**5**) cations.

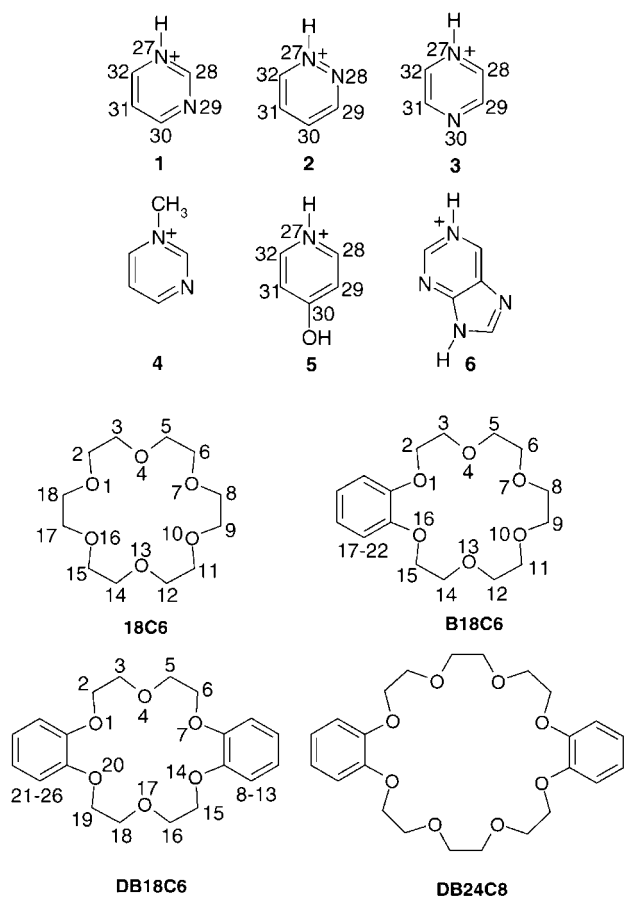
Experimental

General procedures

Pyrimidine, pyridazine, pyrazine, 4-hydroxypyridine, purine, CD₃CN and all crown ethers were commercially avail-

* **Supplementary Data** Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre [deposition numbers CCDC-143610 (18C6-1), CCDC-143611 (B18C6-1), CCDC-143612 (DB18C6-1), CCDC-143613 (DB18C6-3), CCDC-143614 (DB18C6-2) and CCDC-143615 (18C6-5)]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK.

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Scheme 1. Structural formulas and crystallographic numbering of *N*-heteroaromatic cations **1–6** and crown ethers.

able and used without further purification. The solvents were dried and distilled according to the literature procedure [14].

^1H NMR spectra were recorded on a Bruker Avance DPX200 spectrometer operating at 200.130 MHz. ^1H peak positions are reported relative to $[\text{D}_3]\text{CD}_3\text{CN}$ ($\delta = 1.95$ ppm) and TMS ($\delta = 0$ ppm).

ESI (Electrospray Ionisation) mass spectra were recorded on a LCT (Micromass Ltd) Time of Flight mass spectrometer with the OpenLynx 3 data system. The desolvation temperature was 120 °C and N_2 was used as nebuliser and desolvation gas. The sample cone voltage was 20–22 V and the instrument resolution 5000. The sample mixtures for the spectra of the purinium complexes were in the 0.3 mM range and for the other complexes 7–9 mM range. Elemental analysis was carried out with a Perkin-Elmer 2400 analyzer. Melting points were determined with a Thermopan microscope (Reichert, Vienna) and are uncorrected.

The X-ray crystallographic data for DB18C6·**1** and DB18C6·**5** were recorded with an Enraf-Nonius CAD4 diffractometer and for all other complexes with a Nonius Kappa CCD diffractometer. Graphite monochromatised $\text{MoK}\alpha$ radiation [$\lambda(\text{MoK}\alpha) = 0.71073$ Å] and a temperature of 173.0 ± 0.1 K were used in all cases except for DB18C6·**5**, which was measured using graphite monochromatised $\text{CuK}\alpha$ radiation [$\lambda(\text{CuK}\alpha) = 1.54178$ Å] and a temperature of 223.0 ± 0.1 K. The CCD data were processed with Denzo-SMN v0.93.0 [15] and all reflections were corrected for

Lorentz and polarisation effects. An absorption correction was not applied. The structures were solved by direct methods (SHELXS-97 [16]) and refined on F^2 (SHELXL-97 [17]). The hydrogen atoms were calculated to their idealised positions with isotropic temperature factors (1.2 times the carbon temperature factor) and refined as riding atoms. The hydrogens of the water molecule in the B18C6·**1** structure could not be located. Three oxygens of one of the perchlorate anions in 18C6·**1** are disordered over two sites with occupancies of 0.590 and 0.410. One fluorine atom of BF_4^- in the complex DB18C6·**5** is disordered over two positions (site occupancies 0.728 and 0.272).

Preparation of salts

The perchlorate salts (**1–3** and **6**) were prepared by treating the base with 60% perchloric acid [18]. 1-Methylpyrimidinium iodide (**4**) and 4-hydroxypyridinium tetrafluoroborate (**5**) were prepared according to the literature procedures [19, 20].

Pyrimidinium perchlorate (1): White solid. Yield 94%. Mp. 182–185 °C decomp. (192 °C [18]). ^1H NMR (CD_3CN): $\delta = 8.1$ (dt, 1H), 9.2 (d, 2H), 9.5 (s, 1H), 13.5 (broad, NH). $\text{C}_4\text{H}_5\text{ClN}_2\text{O}_4$ (180.55): calcd C 26.61, H 2.79, N 15.52; found C 26.38, H 2.45, N 15.35.

Pyridazinium perchlorate (2): White solid. Yield 88%. Mp. 250 °C decomp. ^1H NMR (CD_3CN): $\delta = 8.5$ (d, 1H), 8.5 (d, 1H), 9.5 (t, 2H) 15.0 (broad, NH). $\text{C}_4\text{H}_5\text{ClN}_2\text{O}_4$ (180.55): calcd C 26.61, H 2.79, N 15.52; found C 26.64, H 2.90, N 15.36.

Pyrazinium perchlorate (3): White solid. Yield 93%. Mp. 189–192 °C. ^1H NMR (CD_3CN): $\delta = 9.1$ (s, 4H). $\text{C}_4\text{H}_5\text{ClN}_2\text{O}_4$ (180.55): calcd C 26.61, H 2.79, N 15.52; found C 26.35, H 2.70, N 15.29.

1-Methylpyrimidinium iodide (4): Yellow solid. Yield 52%. Mp. 136–137 °C (equivalent to literature value [19]). ^1H NMR (CD_3CN): $\delta = 4.3$ (s, CH_3 , 3H), 8.1 (t, 1H), 9.1 (dd, 1H), 9.4 (dd, 1H), 9.5 (s, 1H). $\text{C}_5\text{H}_7\text{IN}_2$ (222.02): calcd C 27.05, H 3.18, N 12.62; found C 27.27, H 3.08, N 12.45.

Purinium perchlorate (5): White solid. Yield 58%. Mp. 212–215 °C decomp. ^1H NMR (CD_3CN): $\delta_{\text{H}} = 8.8$ (s, 1H), 9.2 (s, 1H), 9.3 (s, 1H). $\text{C}_5\text{H}_5\text{ClN}_4\text{O}_4$ (220.57): calcd C 27.23, H 2.28, N 25.40; found C 27.31, H 2.18, N 25.20.

4-Hydroxypyridinium tetrafluoroborate (6): Beige solid. Mp. 88–92 °C decomp. ^1H NMR (CD_3CN): $\delta_{\text{H}} = 7.3$ (d, 2H), 8.4 (d, 2H), 10.3 (broad, OH), 11.9 (NH). $\text{C}_5\text{H}_6\text{BF}_4\text{NO}$ (182.91): calcd C 32.83, H 3.31, N 7.66; found C 32.92, H 3.09, N 7.60.

Preparation of complexes

The complexes were prepared by dissolving the perchlorate salt and the crown ether (1 : 1 ratio) separately in a minimum

amount of hot acetonitrile and then combining the solutions. The purinium perchlorate is weakly soluble in acetonitrile, therefore complex (DB18C6)₂-**6** was prepared by mixing the solid guest and host and then dissolving the mixtures in acetonitrile. The complexes precipitated soon after mixing or after the addition of diethyl ether. Attempts to isolate solid complexes DB18C6-**4**, DB18C6-**5** and DB24C8-**6** failed.

DB18C6-1: Yellow solid. Yield 68%. Mp. 180–183 °C. ¹H NMR (CD₃CN): δ_H = 3.9 (m, OCH₂, 8H), 4.1 (m, OCH₂, 8H), 6.9 (s, aryl, 8H), 8.0 (dt, pyrimidinium, 1H), 9.2 (dd, pyrimidinium, 2H), 9.5 (s, pyrimidinium, 1H). C₂₄H₂₉ClN₂O₁₀ (540.95, 1 : 1 host–guest): calcd C 53.29, H 5.40, N 5.18; found C 53.01, H 5.16, N 5.09.

B18C6-1: Pale yellow solid. Yield 80%. Mp. 90–92 °C. ¹H NMR (CD₃CN): δ_H = 3.62 (s, OCH₂, 4H), 3.64 (s, OCH₂, 8H), 3.8 (m, OCH₂, 4H), 4.1 (m, OCH₂, 4H), 6.9 (s, aryl, 4H), 8.0 (dt, pyrimidinium, 1H), 9.2 (dd, pyrimidinium, 2H), 9.6 (s, pyrimidinium, 1H). C₂₀H₃₀ClN₂O_{10.5} (501.91, 1 : 1 : 0.5 host–guest–water): calcd C 47.86, H 6.02, N 5.58; found C 47.63, H 5.84, N 5.98.

18C6-1: White solid. Yield 43%. Mp. 67–68 °C. ¹H NMR (CD₃CN): δ_H = 3.5 (s, OCH₂, 24H), 8.1 (dt, pyrimidinium, 1H), 9.3 (d, pyrimidinium, 2H), 9.6 (s, pyrimidinium, 1H). C₈₂H₁₄₄Cl₆N₁₄O₅₁ (2354.80; 4.5 : 6 : 2 host–guest–solvent, see the crystal structure): calcd C 41.83, H 6.16, N 8.33; found C 41.39, H 5.60, N 8.32.

DB18C6-2: Yellow solid. Yield 77%. Mp. 210–215 °C decomp. ¹H NMR (CD₃CN): δ_H = 3.9 (m, OCH₂, 8H), 4.1 (m, OCH₂, 8H), 6.9 (s, aryl, 8H), 8.4 (dd, pyridazinium, 2H), 9.5 (dd, pyridazinium, 2H). C₂₄H₂₉ClN₂O₁₀ (540.95, 1 : 1 host–guest): calcd C 53.29, H 5.40, N 5.18; found C 53.33, H 5.29, N 5.14.

DB18C6-3: Yellow solid. Yield 51%. Mp. 158–162 °C. ¹H NMR (CD₃CN): δ_H = 3.9 (m, OCH₂, 8H), 4.1 (m, OCH₂, 8H), 6.9 (s, aryl, 8H), 9.1 (s, pyrazinium, 4H). C₂₄H₂₉ClN₂O₁₀ (540.95, 1 : 1 host–guest): calcd C 53.29, H 5.40, N 5.18; found C 53.57, H 5.06, N 4.91.

(DB18C6)₂-6: White solid. Yield 65%. Mp. 153–157 °C. ¹H NMR (CD₃CN): δ_H = 3.9 (s, OCH₂, 16H), 4.1 (m, OCH₂, 16H), 6.9 (s, aryl, 16H), 8.82 (s, purinium, 1H), 9.16 (d, purinium, 1H), 9.30 (d, purinium, 1H). C₄₇H₅₈ClN₅O₁₇ (2 : 1 : 1 : 1 host–guest–acetonitrile–water, 1000.45): calcd C 56.43, H 5.84, N 7.00; found C 56.43, H 5.28, N 6.71.

Stability constant determination by ¹H NMR titration

A standard solution of a guest in CD₃CN was prepared with a concentration of (1–2) × 10^{−3} M, just sufficient to give an observable NMR signal. A series of crown ether solutions (0.01–0.2 M) were made by weighing out an appropriate amount of crown ether. A 1–2 mL portion of the standard solution of the guest was then added and the flask was re-weighed. The spectra were measured immediately after

Table 1. Stability constants of the complexes between crown ethers and six-membered *N*-heteroaromatic cations in CD₃CN solution at 30 °C.

Complex	<i>K</i> /dm ³ mol ^{−1}	Δδ _C /ppm ^a	<i>r</i> ² ^b
DB18C6- 1	103 ± 5	−0.343 ± 0.006	0.996
B18C6- 1	224 ± 7	0.195 ± 0.001	0.997
18C6- 1	349 ± 35	0.22 ± 0.004	0.989
DB24C8- 1	60 ± 4	0.43 ± 0.02	0.996
DB18C6- 2	162 ± 3	−0.347 ± 0.003	0.999
DB18C6- 3	39 ± 2	−0.25 ± 0.01	0.997
DB18C6- 4	10 ± 3	0.10 ± 0.01 ^c	0.984
DB18C6- 5	154 ± 8	0.197 ± 0.004	0.994
DB24C8- 5	107 ± 2	−0.260 ± 0.002	0.999
DB18C6- 6	38 ± 5 ^d	−0.25 ± 0.02	0.991

^a Calculated maximum upfield/downfield shifts (Δδ_C) for the interaction of the crown ethers and aromatic cations in 1 : 1 complexation.

^b Regression correlation (*r*²) for the Benesi-Hildebrandt plot.

^c The small Δδ_C may lead to an inaccurate stability constant value.

^d The stability constant has been measured at 25 °C.

dissolving and mixing of the samples at a constant temperature. The stability constants for 1 : 1 complexation were calculated from the NMR chemical shifts of the Benesi-Hildebrand plot using the least-squares line-fitting procedure [21].

Results and discussion

Complexation in solution

The complexation in solution was studied by determining the stability constants in acetonitrile solution by ¹H NMR titration (Table 1). The 1 : 1 stoichiometry of the complexes in solution was proved by the linear dependence of the ¹H NMR chemical shifts as a function of the host concentration (1/[crown ether]) [22] and by ESI mass spectrometry. The complexes having a possibility for hydrogen bonding have higher stability constants indicating that the complexation of crown ethers and *N*-heteroaromatic cations is mainly caused by the hydrogen bonding except for 1-methylpyrimidinium (**4**), which does not have a N–H hydrogen bond donating site. Interestingly, six-membered cations form systematically more stable complexes than five-membered cations [12, 13]. The solvent effects of these experiments are difficult to estimate and are not discussed. Acetonitrile, however, can also form hydrogen bonds with the studied cations and can therefore effect the strength of the complexation.

The stability constants of the pyrimidinium (**1**) complexes DB18C6-**1**, B18C6-**1**, 18C6-**1** and DB24C8-**1** (Table 1) are clearly higher than the respective values of the imidazolium complexes [12, 13] decreasing in the order 18C6 > B18C6 > DB18C6. The decreasing trend is in agreement with the stabilities of the corresponding imidazolium (Table 2, [12, 13]) and pyridinium [11] complexes and is associated with the relative hydrogen bonding capability of ether and anisole type oxygen atoms. Anisole type oxygens are less basic and obviously do not participate in H-bonding in

Table 2. Stability constants of the complexes between crown ethers with five-membered *N*-heteroaromatic cations in CD₃CN solution at 30 °C [13].

Complex	$K/\text{dm}^3 \text{mol}^{-1}$
DB18C6-Imidazolium	54 ± 2
B18C6-Imidazolium	59 ± 1
18C6-Imidazolium	81 ± 1
DB21C7-Imidazolium	24 ± 2
DB24C8-Imidazolium	22 ± 2
DB18C6-1-Me-imidazolium	35 ± 3
DB18C6-1-Ph-imidazolium	32 ± 1
DB18C6-Pyrazolium	130 ± 3
DB18C6-1,2,4-Triazolium	37 ± 3
DB18C6-Thiazolium	65 ± 2

these complexes. The stability constants reflect the number of ether type oxygens.

The stability constant of 18C6-**1** (350 dm³ mol⁻¹) is significantly larger than the respective values of the pyridinium (113 dm³ mol⁻¹) [11] and imidazolium (81 dm³ mol⁻¹, Table 2) [12, 13] complexes. The stability constant of 18C6-**1** has been calculated at lower host concentrations (linear B-H-plot), since at higher concentrations deviation from linearity is observed. ESI MS results, though, indicate 1 : 1 stoichiometry in solution. However, for reasons not fully understood, an exceptional 3 : 4 host-guest stoichiometry is observed in the solid state. Hydrogen bonding is the main binding force in 18C6 complexes and thus the stability of these complexes correlates with the acidity constants of the heterocycles (pK_a 20 °C in water: pyrimidine 1.23, pyridine 5.23, imidazole 7.00) [23]. The hydrogen bonding distances of the crystal structures also supports this since the N...O distances of 18C6-pyrimidinium (**1**) [2.73–2.79 Å] are on the average shorter than the corresponding distances of the 18C6-imidazolium complex [2.75–3.10 Å] [12, 13].

Like 18C6-**1**, B18C6-**1** also is more stable than the corresponding pyridinium and imidazolium complexes [B18C6-**1** 224 dm³ mol⁻¹, B18C6-pyridinium 96 dm³ mol⁻¹ and B18C6-imidazolium 59 dm³ mol⁻¹ (Table 2)]. The higher stability constant of B18C6-**1** could be explained by the stronger hydrogen bonding and the participation of π-π/cation-π interactions as is also proved by the solid state structures. Both 18C6 and B18C6 can form hydrogen bonds with ether oxygen atoms more freely since they are more flexible than e.g., DB18C6.

The stability constants of DB18C6-diazinium complexes decrease according to the relative position of the ring nitrogen atoms in the order ortho- > meta- > para-diazinium (162 dm³ mol⁻¹ for DB18C6-**2**, 103 dm³ mol⁻¹ for DB18C6-**1** and 39 dm³ mol⁻¹ for DB18C6-**3**). The H-bonded N–O (N–H...O) distances in the crystal structures decrease in the same order (DB18C6-**2** 2.68 Å; DB18C6-**1** 2.83 Å; DB18C6-**3** 2.97 Å). The same trend was also observed in complexes of heterocyclic bases with phenol and its derivatives [6–8].

4-Hydroxypyridinium (**5**) forms an equally strong DB18C6 complex ($K = 38 \text{ dm}^3 \text{ mol}^{-1}$) as pyrazinium (**3**, $K = 39 \text{ dm}^3 \text{ mol}^{-1}$) and pyridinium (33 dm³ mol⁻¹) [11] cations. In solution this indicates a preferred complexation via N–H...O hydrogen bonding without a significant participation of the OH group in 1 : 1 complexes. However, the stability constant measurements showed some deviations from 1 : 1 stoichiometry at higher host concentrations and ESI MS studies indicated also formation of complex units with 2 : 1 host-to-guest stoichiometry. The crystal structure, though, showed 1 : 1 complexation stoichiometry.

The stability of the DB18C6-*N*-methylpyrimidinium (**4**) complex is low (10 dm³ mol⁻¹), but correlates well with the stabilities of the *N*-methylpyridinium (9 dm³ mol⁻¹) [11] and tropylium (C₇H₇⁺, 6 dm³ mol⁻¹) [9, 10] complexes. In all these cases, there is no possibility for N–H...O hydrogen bonding, instead cation-π interactions are possible. Substituted 1-methyl and 1-phenylimidazolium complexes, which have possibilities also for hydrogen bonding, gave clearly higher stability constants (35 dm³ mol⁻¹ and 32 dm³ mol⁻¹, respectively) [12, 13].

The stabilities of both purinium complexes, DB18C6-**6** (lower host concentration, 1 : 1 stoichiometry, $K = 154 \text{ dm}^3 \text{ mol}^{-1}$) and DB24C8-**6** ($K = 107 \text{ dm}^3 \text{ mol}^{-1}$), are equal to the strongest six-membered cation complexes. At the higher host concentrations the tendency of DB18C6-**6** to form a 2 : 1 complex is observed as a strong deviation from the linearity of the Benesi–Hildebrand plot. The 2 : 1 stoichiometry was observed also in the solid state, when an interesting dimeric capsule is formed [24]. Similar behaviour is not observed with the larger DB24C8 host, which can completely fold over a guest as was observed with the corresponding tropylium complex [9, 10]. The differences in complexation of purinium cation can also be seen in the chemical shift changes of the ring proton signals in the ¹H NMR titration. The most significant shift in DB18C6-**6** is the downfield shift of proton H-6, while in DB24C8-**6** upfield shifts of H-2 and H-8 are observed.

ESI MS studies support the complexation behaviour of the purinium cation in solution and in the solid state [24]. ESI MS spectra of the purinium complexes show that DB18C6-**6** [2 : 1 host/guest stoichiometry, m/z 841 (39%)] has a greater tendency to form a 2 : 1 host-to-guest complex than DB24C8-**6** [m/z 1018 (1%)].

Solid state complexes

The crystal structures of the DB18C6-**1**, B18C6-**1** and 18C6-**1** complexes were determined, while attempts to obtain suitable crystals from DB24C8-**1** failed. The structures of the DB18C6 complexes of pyridazinium (**2**), pyrazinium (**3**) and 4-hydroxypyridinium (**5**) were determined as comparison to the pyrimidinium structure. Suitable single crystals for X-ray analysis were obtained by slow evaporation of acetonitrile or use of the vapour diffusion method. The crystal data are presented in Table 3. The fractional coordinates, bond distances and angles are deposited with the Cambridge Crystallographic Data Centre [deposition numbers 143610

Table 3. The crystal data for crown ether complexes of six-membered N-heteroaromatic cations.

Compound	18C6-1	B18C6-1	DB18C6-1	DB18C6-2	DB18C6-3	DB18C6-5
Formula	4.5C ₁₂ H ₂₄ O ₆ ·6C ₃ H ₅ N ₂ ⁺ ·6ClO ₄ ⁻ ·3C ₂ H ₃ N	C ₁₆ H ₂₄ O ₆ ·C ₄ H ₅ N ₂ ⁺ ·ClO ₄ ⁻ ·0.5 H ₂ O	C ₂₀ H ₂₄ O ₆ ·C ₄ H ₅ N ₂ ⁺ ·ClO ₄ ⁻	C ₂₀ H ₂₄ O ₆ ·C ₄ H ₅ N ₂ ⁺ ·ClO ₄ ⁻	C ₂₀ H ₂₄ O ₆ ·C ₄ H ₅ N ₂ ⁺ ·ClO ₄ ⁻	C ₂₀ H ₂₄ O ₆ ·C ₅ H ₅ NOH ⁺ ·BF ₄ ⁻
Formula weight	2395.9	510.9	540.94	540.94	540.94	543.31
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	C c (No. 9)	C c (No. 9)	C c (No. 9)	P 21/n (No. 14)
<i>a</i>	13.0466(3) Å	7.0172(3) Å	17.653(5) Å	17.758(1) Å	17.9445(7) Å	11.175(2) Å
<i>b</i>	18.5334(3) Å	12.5548(4) Å	13.281(4) Å	13.863(1) Å	13.3172(5) Å	38.666(8) Å
<i>c</i>	25.2096(4) Å	13.9552(5) Å	12.884(7) Å	12.9741(6) Å	12.7757(4) Å	12.471(2) Å
α	100.673(1)°	83.176(2)°	90°	90°	90°	90°
β	98.4906(8)°	79.096(2)°	126.53(3)°	129.791(4)°	127.322(2)°	110.82(3)°
γ	99.938(1)°	77.852(2)°	90°	90°	90°	90°
Volume	5797.8(2) Å ³	1176.21(8) Å ³	2427(2) Å ³	2454.2(3) Å ³	2427.9(2) Å ³	5036.8(2) Å ³
Z	2	2	4	4	4	8
Density (calculated)	1.372 Mg·m ⁻³	1.437 Mg·m ⁻³	1.480 Mg·m ⁻³	1.464 Mg·m ⁻³	1.480 Mg·m ⁻³	1.433 Mg·m ⁻³
Absorption coefficient	0.244 mm ⁻¹	0.225 mm ⁻¹	0.220 mm ⁻¹	0.218 mm ⁻¹	0.220 mm ⁻¹	1.049 mm ⁻¹
F(000)	2532	536	1136	1136	1136	2272
Refl. collected/unique	36249/26555	8270/5470	2195/2195	6550/4742	7126/4844	10726/10260
Data/restraints/parameters	26555/0/1436	5470	2195/2/334	4742/2/335	4844/2/335	10260/0/698
Goof	1.015	1.044	1.093	1.068	1.049	1.047
Final <i>R</i> indices (<i>I</i> > 2σ <i>I</i>)	0.069/0.134	0.055/0.138	0.026/0.065	0.097/0.233	0.041/0.084	0.064/0.185
<i>R</i> indices (all data)	0.147/0.164	0.082/0.152	0.029/0.068	0.137/0.256	0.055/0.090	0.108/0.226
Largest diff. peak and hole	0.575/−0.387 e.Å ⁻³	0.249/−0.656 e.Å ⁻³	0.172/−0.290 e.Å ⁻³	0.948/−0.503 e.Å ⁻³	0.219/−0.240 e.Å ⁻³	0.709/−0.503 e.Å ⁻³

(18C6-1), 143611 (B18C6-1), 143612 (DB18C6-1), 143613 (DB18C6-3), 143614 (DB18C6-2) and 143615 (18C6-5).

In the crystalline state the DB18C6 complexes of unsubstituted cations show a remarkable resemblance to one another and also to the previously determined pyridinium and five-membered *N*-heteroaromatic cation complexes [12, 13]. All these complexes crystallise in an acentric monoclinic space group (*Cc*) with very similar unit cell dimensions and nearly isomorphous structures. The only exception is the 4-hydroxypyridinium (**5**) complex, which crystallises in a centric space group P2₁/n. The B18C6-1 and 18C6-1 complexes do not have such a close resemblance to the structures of the respective imidazolium complexes [13], but they crystallise in a centrosymmetric triclinic space group (*P*-1), with some amount of solvent included in the crystal lattice.

Hydrogen bonding is the dominant complexing interaction also between DB18C6 and six-membered nitrogen-containing cations. However, the π - π interactions seem to have somewhat more significance than with smaller cations, owing to the larger size of the guest. The distance between the centroids of the closest phenyl ring of the host and the guest vary from 3.7 to 4.0 Å, while in five-membered rings the distances are approximately 4.1 Å [12, 13]. These values are in agreement with the respective values of the DB18C6-pyridinium complexes [11].

The hydrogen-bonding pattern is slightly different from the pattern of the five-membered cations since there is only one hydrogen bond donating site in six-membered cations in contrast to two possible donating sites of the five-membered cations [12, 13]. Therefore hydrogen bonding to two adjacent hosts is possible only in the case of 4-hydroxypyridinium (**5**). The shortest hydrogen bonds of the unsubstituted six-membered cations are observed with pyridazinium (**2**) [N(27)···O(17)

= 2.683(9) Å, N(27)···O(20) = 3.146(9) Å] and the longest with pyrazinium (**3**) [N(27)···O(17) = 2.973(3) Å and N(27)···O(14) = 3.008(3) Å]. The hydrogen bonds of pyrimidinium (**1**) are of intermediate length being N(27)···O(17) = 2.826(3) Å and N(27)···O(20) = 3.173(3) Å. A remarkable difference in hydrogen bonding of the DB18C6-2 complex compared to the other two DB18C6 complexes is also observed. Possible π - π stacking interactions were observed in two closely related compounds of host DB18C6. Interestingly enough, whereas these interactions are within the H-bonded host-guest associates in DB18C6-1 (1:1), they are 'intercomplex' by nature in the related DB18C6-3 (1:1) compound. In the pyridazinium complex (DB18C6-2), however, both hydrogen bonding and π - π interaction are intracomplex by nature (Figure 1). This clearly indicates that the pyridazinium complex is stronger than the other two complexes as suggested also by the measurement of the stability constant. Additionally, in all these complexes relatively strong C-H···O hydrogen bonds [3.17–3.67 Å] between the guest and the host stabilise the complex.

All DB18C6 complexes with unsubstituted six-membered heterocycles are 1:1 complexes, which owing to the packing in polar, one-dimensional arrays can only be crystallographically described as 2:2 complexes [12]. The 4-hydroxypyridinium (**5**) complex, however, is also formally a 2:2 complex in the solid state i.e., the asymmetric unit contains two hosts in slightly different conformations and two guests orienting differently in the cone of the DB18C6. The reason for this can be rationalised by investigating the hydrogen bonds between the guest and the host or the BF₄⁻ anion. The 4-hydroxypyridinium is capable of forming hydrogen bonds to two adjacent hosts. The hydroxyl groups, which are oriented outside of the cavity of

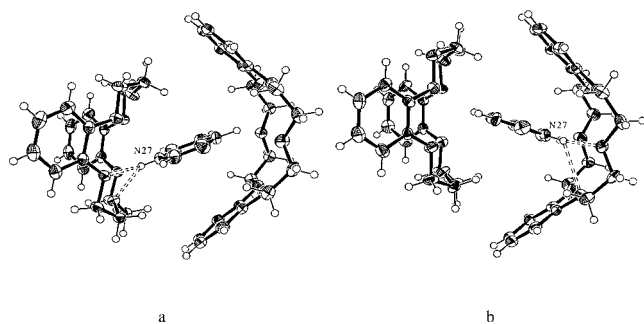


Figure 1. DB18C6-1 (a) forms intercomplex hydrogen bonds (shown as broken bars), while the hydrogen bonds of DB18C6-2 (b) are intracomplex by nature. π - π and C-H...O interactions stabilise the complex. The perchlorate anions are excluded and hydrogen bond donating nitrogens are labelled for clarity.

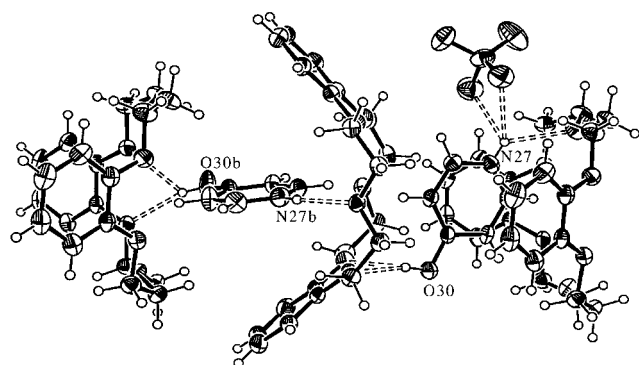


Figure 2. Hydrogen bonding of the DB18C6-5 complex. One of the cations forms hydrogen bonds (shown as broken bars) both to the host and to the anion. Another anion is excluded for clarity.

the host, form strong hydrogen bonds to the adjacent host [O(30)...O(1B) = 2.739(3) Å, O(30)...O(20B) = 2.895(3) Å and O(30B)...O(1) = 2.844(3) Å, O(30B)...O(20) = 2.844(3) Å] (Figure 2). The nitrogen atoms, on the other hand, orient towards the cavity also forming hydrogen bonds to the other host [N(27)...O(17*) = 2.986(3) Å (* = x + 1, y z + 1) and N(27B)...O(4B) = 2.888(3) Å]. However, one nitrogen is also at the hydrogen bonding distance to one of the BF₄⁻ anions [N(27)...F(203) = 2.889(4) Å and N(27)...F(204) = 2.995(4) Å]. Such interaction between the cation and the anion was not observed with other six- or five-membered cations [11–13]. The interaction between the anion and the cation may be considered as a probable reason for the difference in packing of the 4-hydroxypyridinium complex compared to other DB18C6 complexes. In this case, although columnar packing is observed, the columns do not pack one-dimensionally but centrosymmetrically.

Based on the structural similarities of the 4-hydroxypyridinium (5) and purinium (6) guests (the distance between the hydrogen bonding sites of the 4-hydroxypyridinium is almost the same as in purinium, being 4.03 Å and 3.92 Å, respectively), they probably could be expected to be capsulated in similar ways [24]. However, the 4-hydroxypyridinium does not form a capsule-like dimer like purinium. The reason for this is most likely the smaller dimensions of the guest and the unfavourable spatial orientation of the hydrogen bond donating hydroxyl group.

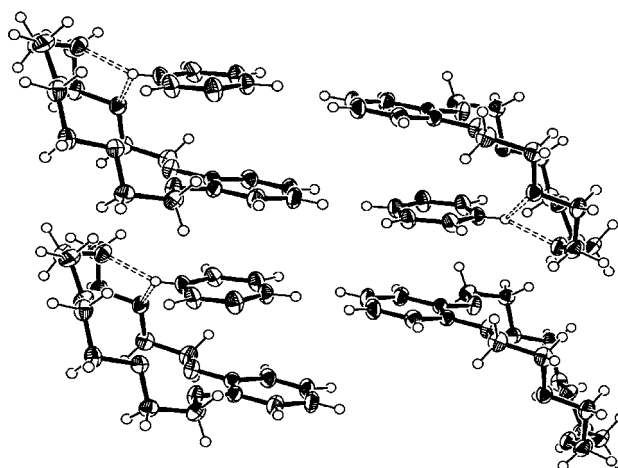


Figure 3. Packing of B18C6-1 is stabilised by the hydrogen bonding and π - π interactions between the hosts and the guests as well as the π - π interactions between the adjacent columns.

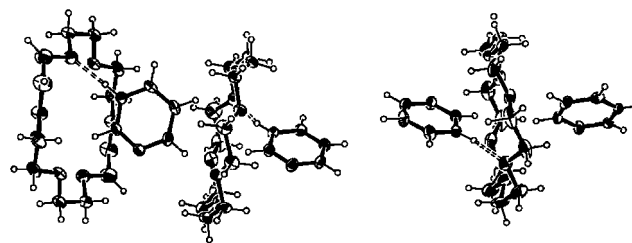


Figure 4. A view of the 18C6-1 complex showing only the unsymmetrical part of the crystal lattice. Instead of the normal host-guest-host-guest order some parts of the columns are in the order host-guest-guest-host. Anions and acetonitrile molecules are excluded for clarity.

Due to the more flexible nature of B18C6 and 18C6 their pyrimidinium complexes are not isomorphous to the respective imidazolium complexes [13]. In B18C6-imidazolium no indication of π - π interaction as a complexing force in the solid state was observed since the distance between the centroids of the phenyl ring of the host and the guest is \sim 4.7 Å. In the B18C6-pyrimidinium (1) complex, however, the distance between the centroids of the phenyl ring of the host and the guest is 3.84 Å, therefore indicating the significance of π - π interaction for the complexation. In addition to the π - π interactions the hydrogen bonds N(27)...O(10) = 2.751(3) Å and N(27)...O(13) = 3.083(3) Å stabilise the complexation.

The π - π interactions are also important for the packing of the B18C6 complex. The complexes do not form similar distinctive columns to the DB18C6 complexes or B18C6-imidazolium [13] but the guests are π -stacked between the hosts (Figure 3). In addition the adjacent hosts are relatively close to each other, the shortest distance between the aromatic units being about 3.9 Å. The interstices in the crystal lattice are filled with perchlorate anions and water molecules, which are at the hydrogen bonding distance from O(7) of the crown ether [O(100)...O(7) = 2.934(3) Å].

The 18C6-pyrimidinium (1) complex has an exceptional host-to-guest ratio of 3:4 in the solid state (the asymmetric unit contains four and a half host molecules, six cations and perchlorate anions and three acetonitrile molecules).

All guests are hydrogen bonded to the adjacent hosts with equal, strong hydrogen bonds [2.707(4)–2.796(3) Å]. The complexes form centrosymmetrical columns, basically similar to the other columnar complexes, but due to the uneven ratio of the hosts and guests there is an exception of the symmetry in some columns. Instead of the normal host–guest–host–guest order, a part of the column is in the order of host–guest–guest–host (Figure 4).

Conclusions

The studied six-membered *N*-heteroaromatic cations form 1 : 1 H-bonded host–guest associates with crown ethers 18C6, B18C6, DB18C6 and DB24C8. The excess of the crown ether does not affect the average of the complexation stoichiometry, only the DB18C6-purinium (**6**) prefers 2 : 1 complexation. Hydrogen bonding is the main interaction in the complex formation, but cation- π interactions can also be observed in the crystal structures.

The X-ray crystallographic studies show isomorphous structures and close resemblance between all DB18C6 complexes regardless of whether the cation is five- [12, 13] or six-membered. With B18C6 and 18C6 complexes such behaviour is not observed due to the more flexible nature of the hosts. The crystal structures prove hydrogen bonding to be the dominating complexation force, but the importance of π - π interactions is also obvious in the DB18C6 and B18C6 complexes. The extraordinary host:guest ratio of 3 : 4 caused by an exception in the columnar packing was observed in the 18C6-**1** complex.

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