

4-Methoxyanilinium tetrafluoro-
borate–dibenzo-18-crown-6 (1/1)

Xue-qun Fu, Yong-le Yang and Qiong Ye*

Ordered Matter Science Research Center, Southeast University, Nanjing 210096,
People's Republic of China

Correspondence e-mail: fuxuequn222@163.com

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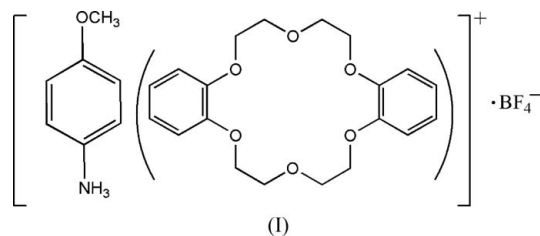
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In the structure of the complex of dibenzo-18-crown-6 [systematic name: 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacos-1(26),9,11,13,22,24-hexaene] with 4-methoxyanilinium tetrafluoroborate, $C_7H_{10}NO^+ \cdot BF_4^- \cdot C_{20}H_{24}O_6$, the protonated 4-methoxyanilinium ($MB-NH_3^+$) cation forms a 1:1 supramolecular rotator–stator complex with the dibenzo-18-crown-6 molecule *via* $N-H \cdots O$ hydrogen bonds. The $MB-NH_3^+$ group is attached from the convex side of the bowl-shaped crown, in contrast with similar ammonium cations that nest in the curvature of the bowl. The cations are associated *via* $C-H \cdots \pi$ interactions, while the cations and anions are linked by weak $C-H \cdots F$ hydrogen bonds, forming cation–crown–anion chains parallel to [011].

Comment

Because of their novel coordination modes, crown ethers have been widely used in catalysis, solvent extraction, isotope separation, bionics, materials chemistry, host–guest chemistry and supramolecular chemistry (Clark *et al.*, 1998; Nakamura *et al.*, 1998). Crown ethers have attracted much attention recently due to their ability to form noncovalent hydrogen-bonded complexes with ammonium cations, both in the solid state and in solution (Fender *et al.*, 2002; Kryatova *et al.*, 2004). The structures of organic ammonium RNH_3^+ (crown ether) assemblies in the solid state depend not only on the structure of the cation and the size of the crown ether ring, but also on the nature of the counter-anion. Various types of RNH_3^+ structures ($R = H, CH_3, C_6H_5CH_2, NH_2, etc.$) have been shown to form stable ammonium(crown ether) complexes in the solid state (Akutagawa *et al.*, 2005, 2009). The crown ether supramolecular approach has two advantages (Akutagawa *et al.*, 2008). Firstly, the combination of organic and/or inorganic cations and crown ethers yields diverse molecular rotator structures. Secondly, one-pot synthesis of rotator–stator structures by self-assembly processes through selective cation recognition by crown ethers becomes possible. The ionic radius of NH_4^+ matches the cavity size of six-O crown ethers, and $N-H \cdots O$ hydrogen bonds help to form stable

RNH_3^+ (crown ether) complexes. The potential capacity of dibenzo crowns to form π – π interactions upon stacking seemed to us to be an interesting property that could lead to more stable supramolecular assemblies.



The asymmetric unit of the title compound, (I), contains a 1:1 ($MB-NH_3^+$)(DB[18]crown-6) adduct in the supramolecular cation and a disordered tetrafluoroborate anion (Fig. 1) ($MB-NH_3^+$ is the 4-methoxyanilinium cation and DB[18]crown-6 is dibenzo-18-crown-6). The DB[18]crown-6 molecule possesses a jackknife-type configuration, with a folding angle between the two arene rings of $134.38 (15)^\circ$, indicating that the rings are oriented in the same direction with respect to the crown ether ring. This configuration of the crown itself is similar to that observed in the anilinium ($Ph-NH_3^+$) and adamantylammonium ($AD-NH_3^+$) complexes of DB[18]crown-6 (Akutagawa *et al.*, 2008). The arene rings are essentially planar, with average deviations of the C atoms from the arene planes of 0.003 \AA for both benzo groups. The six O atoms of the crown ring are almost coplanar, with an r.m.s. deviation of 0.036 \AA .

In the supramolecular cation of (I), the ammonium N atom is in a backward perching position on the convex side of the bowl, lying 0.77 \AA from the O_6 plane and with the $C-N$ bond of the $MB-NH_3^+$ group perpendicular to the mean O-atom plane, rather than in the nesting position (*i.e.* on the concave side of the bowl). By contrast, in the $Ph-NH_3^+$ and $AD-NH_3^+$ complexes, the amine is found in the nesting location (Akutagawa *et al.*, 2008).

The supramolecular cation of (I) is constructed from three trifurcated ammonium–crown $N-H \cdots O$ hydrogen bonds,

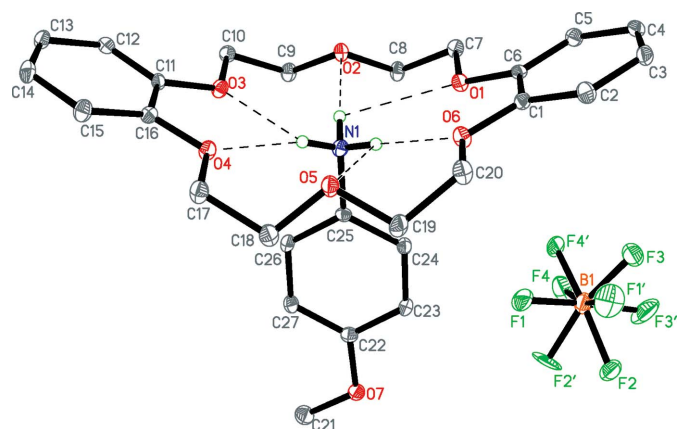


Figure 1

The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. N-Bound H atoms are shown as small spheres of arbitrary radii; all other H atoms have been omitted for clarity. Dashed lines indicate $N-H \cdots O$ hydrogen bonds. The BF_4^- anion is disordered over two orientations, with F-atom occupancies of 0.905 (3) (unprimed) and 0.095 (3) (primed).

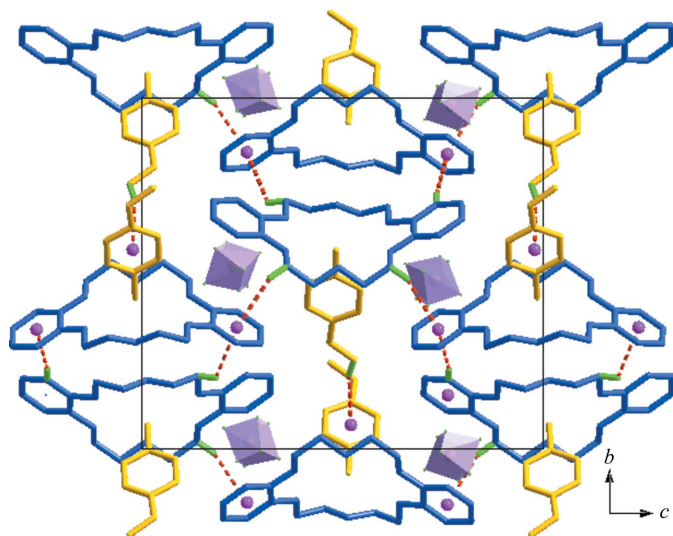


Figure 2
A view of the packing of (I) along the *a* axis. Dashed lines indicate C—H... π interactions. Both orientations of the disordered BF_4^- anions are shown.

each with one strong (H...O *ca* 2.0 Å) linear interaction and two much weaker (H...O *ca* 2.5 Å) acute interactions (Table 1). A similar pattern was observed in the 18-crown-6 complex of propane-1,3-diaminium (Zhao & Qu, 2010). The N...O distances are consistent with similar interactions in other ammonium complexes of DB[18]crown-6 (Akutagawa *et al.*, 2005, 2008).

In the packing of (I), the jackknife-shaped supramolecular cations are arranged in slanting pairs, wherein the dihedral angle between adjacent O_6 planes is *ca* 64.61 (3)°. In addition to N—H...O hydrogen bonds, C—H... π interactions are the main molecular interaction. The pairwise face-to-face (MB- NH_3^+)(DB[18]crown-6) cations are linked by C—H... π interactions, with C...centroid distances in the range 3.511 (4)–3.878 (4) Å, forming one-dimensional chains along the *b* axis (Fig. 2). The disordered tetrafluoroborate anions run between these chains and link them by weak C—H...F hydrogen bonds (Table 1), forming cation–crown–anion chains parallel to [011].

It is interesting that the molecular configuration and packing in (I) are quite different from those found in the related (Ph- NH_3^+)(DB[18]crown-6)[Ni(dmit)₂] and (AD- NH_3^+)(DB[18]crown-6)[Ni(dmit)₂][−] salts (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate; Akutagawa *et al.*, 2008). In the (Ph- NH_3^+)(DB[18]crown-6) and (AD- NH_3^+)(DB[18]crown-6) complexes, the $-\text{NH}_3^+$ groups are in the forward perching (nesting) position, and the cation and anion layers are arranged alternately with a uniform stacking, in which the supramolecular cations are arranged in the same direction. These differences may be due to the BF_4^- anion, which is relatively small [compared with [Ni(dmit)₂]] for embedding large supramolecular cations in the crystal structure. The BF_4^- anions lack the ability to form π – π interactions but offer better hydrogen-bond acceptors to the C—H groups. Such a feature would further support the observed behaviour.

Experimental

4-Methoxyaniline (0.25 g, 2 mmol) was dissolved in methanol (10 ml), to which tetrafluoroboric acid in aqueous solution (0.44 g, 40% *w/w*) was then added slowly with stirring over a period of 20 min. During this reaction, the pH of the solution gradually changed to *ca* 7. Dibenzo-18-crown-6 (0.72 g, 2 mmol) was added and the mixture was heated under reflux for 24 h. The reaction solution was cooled to room temperature and filtered. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation from the filtrate at room temperature after 2 d, giving a yield of *ca* 62%. The crystals were colourless, prismatic and of average size 0.2 × 0.3 × 0.4 mm.

Crystal data

$\text{C}_7\text{H}_{10}\text{NO}^+\cdot\text{BF}_4^-\cdot\text{C}_{20}\text{H}_{24}\text{O}_6$
 $M_r = 571.36$
Orthorhombic, $P2_12_12_1$
 $a = 8.863$ (4) Å
 $b = 16.408$ (7) Å
 $c = 18.806$ (8) Å

$V = 2735$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.12$ mm^{−1}
 $T = 103$ K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(CrystalClear; Rigaku, 2005)
 $T_{\min} = 0.959$, $T_{\max} = 0.977$

30293 measured reflections
3521 independent reflections
3278 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.105$
 $S = 1.16$
3521 reflections
407 parameters
10 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.17$ e Å^{−3}
 $\Delta\rho_{\min} = -0.29$ e Å^{−3}

Table 1

Hydrogen-bond and C—H... π geometry (Å, °).

Cg1, Cg2 and Cg3 are the centroids of the C1–C6, C11–C16 and C22–C27 rings, respectively.

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O1	0.87 (2)	2.45 (2)	2.855 (3)	109 (2)
N1—H1A...O5	0.87 (2)	2.53 (3)	2.881 (3)	103 (2)
N1—H1A...O6	0.87 (2)	1.98 (2)	2.854 (3)	177 (3)
N1—H1B...O3	0.90 (2)	2.48 (2)	2.887 (3)	110 (2)
N1—H1B...O4	0.90 (2)	2.00 (2)	2.880 (3)	165 (3)
N1—H1B...O5	0.90 (2)	2.49 (3)	2.881 (3)	107 (2)
N1—H1C...O1	0.88 (2)	2.51 (3)	2.855 (3)	104 (2)
N1—H1C...O2	0.88 (2)	2.00 (2)	2.886 (3)	177 (3)
N1—H1C...O3	0.88 (2)	2.53 (3)	2.888 (3)	105 (2)
C19—H19A...F1	0.97	2.52	3.139 (4)	121
C7—H7B...F1 ⁱ	0.97	2.52	3.192 (4)	127
C5—H5A...F2 ^j	0.93	2.32	3.222 (4)	163
C26—H26A...F2 ⁱⁱ	0.93	2.41	3.132 (4)	135
C27—H27A...F3 ⁱⁱⁱ	0.93	2.53	3.174 (4)	126
C12—H12A...F4 ⁱⁱⁱ	0.93	2.30	3.192 (4)	161
C7—H7A...Cg2 ^{iv}	0.97	2.95	3.798 (4)	147
C10—H10B...Cg1 ⁱⁱⁱ	0.97	2.96	3.812 (4)	147
C15—H15A...Cg1 ^v	0.93	2.86	3.761 (4)	165
C20—H20B...Cg1 ^v	0.97	2.96	3.511 (4)	117
C21—H21A...Cg3 ^{vi}	0.96	2.95	3.878 (4)	163

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (v) $-x, y + \frac{3}{2}, -z + \frac{3}{2}$; (vi) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

The positional parameters of all C-bound H atoms were calculated geometrically and allowed to ride, with aromatic C—H = 0.93 Å,

crown ether C–H = 0.97 Å and methyl C–H = 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for all other H atoms. All ammonium H atoms were found in a difference Fourier map. However, they were then placed in ideal positions and refined using a rotating model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$, with restraints for the N–H and H···H distances of 0.86 (2) and 1.45 (2) Å, respectively. The tetrafluoroborate anion is disordered over two orientations, with site-occupancy factors of 0.905 (3) (unprimed) and 0.095 (3) (primed). The B–F' distances of the low-occupancy F sites were refined with restraints of 1.39 (2) Å. In the absence of significant anomalous scattering effects, Friedel pairs were merged and the absolute configuration was chosen arbitrarily.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3254). Services for accessing these data are described at the back of the journal.

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