organic compounds

4-Carboxypyridinium perchlorate 18-crown-6 dihydrate clathrate and 4-carboxypyridinium tetrafluoroborate 18-crown-6 dihydrate clathrate

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Mixtures of 4-carboxypyridinium perchlorate or 4-carboxypyridinium tetrafluoroborate and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) in ethanol and water solution yielded the title supramolecular salts, $C_6H_6NO_2^+\cdot ClO_4^-\cdot C_{12}H_{24}O_6\cdot 2H_2O$ and $C_6H_6NO_2^+\cdot BF_4^-\cdot C_{12}H_{24}O_6\cdot 2H_2O$. Based on their similar crystal symmetries, unit cells and supramolecular assemblies, the salts are essentially isostructural. The asymmetric unit in each structure includes one protonated isonicotinic acid cation and one crown ether molecule, which together give a $[(C_6H_6NO_2)(18\text{-crown-6})]^+$ supramolecular cation. N—H···O hydrogen bonds between the protonated N atoms and a single O atom of each crown ether result in the 4-carboxypyridinium cations 'perching' on the 18-crown-6 molecules. Further hydrogen-bonding interactions involving the supramolecular cation and both water molecules form a one-dimensional zigzag chain that propagates along the crystallographic c direction. O—H···O or O—H···F hydrogen bonds between one of the water molecules and the anions fix the anion positions as pendant upon this chain, without further increasing the dimensionality of the supramolecular network.

Comment

Crown ethers have attracted much attention because of their ability to form noncovalent and hydrogen-bonded complexes with ammonium cations in both solid and solution states (Fender et al., 2002; Rieger & Muclring, 2005). 18-Crown-6 and its derivatives exhibit the highest affinity with organic ammonium cations (RNH_3^+) and commonly have a 1:1 stoichiometry (Doxsee et al., 2000; Buschmann et al., 2001; Johnson et al., 2000; Zhao & Qu, 2010). Meanwhile, pyridinecarboxylic acid is an interesting material with which to construct hydrogen-bonded structures with a variety of inorganic anions. The reported crystal structures of pyridinecarboxylate salts involve a variety of hydrogen-bond modes

and interest has also been shown in their phase transition structures and in physical property investigations (Jebas et al., 2006; Chen et al., 2009). In the light of these interesting hydrogen-bonding interactions in crown ether adducts and pyridinecarboxylate salt systems, we synthesized and present herein the structures of the title compounds, 4-carboxypyridinium perchlorate 18-crown-6 dihydrate clathrate, (I), and 4-carboxypyridinium tetrafluoroborate 18-crown-6 dihydrate clathrate, (II). Both contain an adduct of 18-crown-6 and the isonicotinic acid cation. The results provide a new type of interaction in the supramolecular chemistry of crown ethers, different from the hydrogen-bond interactions seen previously between the 4-carboxypyridinium cation and crown ethers (Lamsa et al., 1998).

(I) $X = ClO_4^-$
(II) $X = BF_4^-$
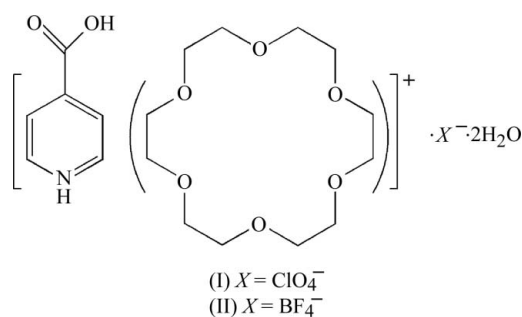
The asymmetric unit of (I) contains one 4-carboxypyridinium cation, one 18-crown-6 molecule, one perchlorate anion and two water molecules (Fig. 1). As the pyridine ring of the isonicotinic acid cation is too large to fit into the 18-crown-6 cavity, no electron density is found inside the crown ether ring in (I). The crown ether and protonated isonicotinic acid components form a 'perching' complex, where the pyridine ring rests above the mean plane defined by the O atoms of the crown ether. The dihedral angle between the plane of the pyridine ring and the mean plane of the crown O atoms is 53.61 (8)°. The N atom of the pyridine ring from the isonicotinic acid cation links to only one O atom of the
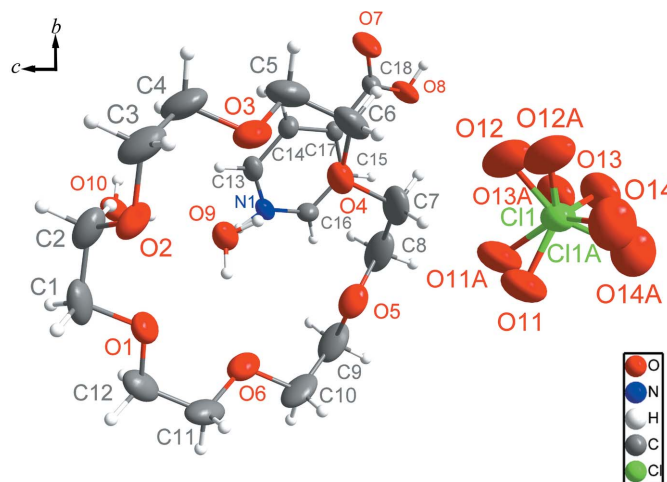
Figure 1
The molecular structure of (I), showing the atom-labelling scheme and the disordered anion. Displacement ellipsoids are drawn at the 30% probability level.
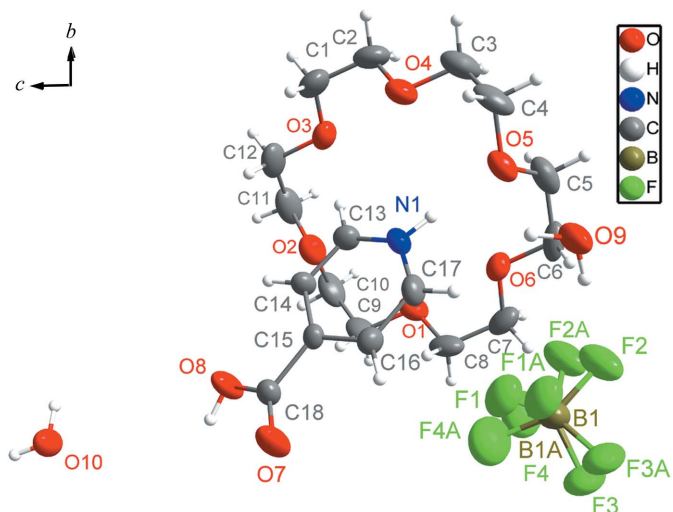
doi:10.1107/S0108270112024912
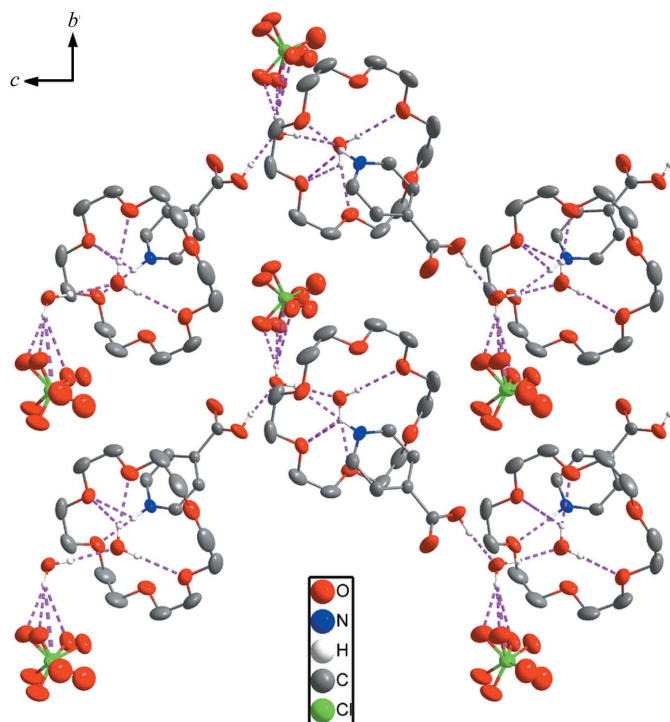
Figure 2
The packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms which are not involved in hydrogen bonds have been omitted.
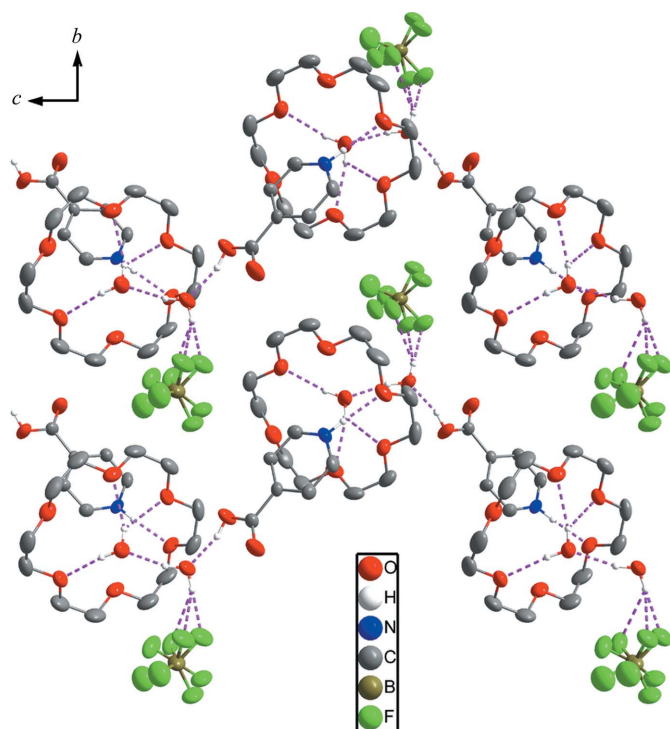

Figure 3
The molecular structure of compound (II), showing the atom-labelling scheme and the disordered anion. Displacement ellipsoids are drawn at the 30% probability level.

crown ether molecule through a short N—H⋯O hydrogen bond (Table 1). The 18-crown-6 rings do not have the normal ideal crown conformation. That is, the O atoms of the 18-crown-6 molecule are not displaced alternately above and below the median plane of the ring. The distances (Å) of the ether O atoms from their mean plane are: O1 −0.223 (2), O2 0.247 (2), O3 0.025 (2), O4 −0.332 (2), O5 0.376 (2) and O6 −0.094 (2). Thus, atoms O3, O4, O5 and O6 are in the usual alternating pattern of crown ether O atoms, but atom O2, which should sit below the mean plane, sits above it. The formation of only one short hydrogen bond (N1—H1⋯O2) may result in the deviation of atom O2 from the plane and contribute to the adoption of the observed non-ideal crown conformation.

In (I), two solvent water molecules are found per formula unit. Whilst each crown ether molecule is coordinated by an isonicotinic acid cation on one side, the other side of the crown is occupied by one of the solvent water molecules. Water atom O9 resides only 1.770 (3) Å from the centre of the crown ether and forms two hydrogen bonds with O atoms of the crown ring (Table 1). It also accepts a hydrogen bond from atom O10 of the second water molecule. The second water molecule is also involved as a hydrogen-bond acceptor with the isonicotinic acid cation as the O—H donor. As a result, a novel one-dimensional zigzag chain, which contains protonated isonicotinic acid cations and 18-crown-6 and solvent water molecules, is formed and extends along the crystallographic *c* direction (Fig. 2).

The asymmetric unit of (II) is composed of a 4-carboxy-pyridinium cation, one crown ether molecule, a tetrafluoro-

borate anion and two water molecules (Fig. 3). It shows essentially the same structural features as described above for (I). The N atom of the isonicotinic acid cation is again in the perching position, lying 2.046 (3) Å from the mean plane of the crown ring, rather than in the nesting position. The adduct in the complex is arranged in such a way that the dihedral angle between the mean plane of the crown ether O atoms and the pyridine ring is 53.13 (8)°, a similar value to that found in (I). Hydrogen-bonding details are given in Table 2. A subtle difference is that, in complex (II), one of the water molecules (O10) could be described as forming four contacts with the crown O atoms, where each water H atom makes a very asymmetric bifurcated bond with two short and two very long contacts (Table 2), whilst in (I) the equivalent long contacts are even longer and so lie outside the range normally considered. What is more, the zigzag chain extending along the crystallographic *c* direction is similar to that in complex (I) (Fig. 4).

The perchlorate and tetrafluoroborate anions are present as counter-ions to the supramolecular $[(C_6H_6NO_2)(18\text{-crown-}6)]^+$ cations. Both anions were modelled as being disordered over two sites. The anions are pendant from the zigzag hydrogen-bonded chain and each forms O—H⋯O/F hydrogen bonds to this chain.

Pyridinium salt complexes with crown ethers have been structurally elucidated by Lamsa *et al.* (1998). These benzene-substituted crown ethers differ from (I) and (II) in the nature of their bond formation. The benzene-substituted complexes are mainly dependent on π–π stacking and cation–π inter-actions, which play significant roles in the complexation between benzene-substituted crown ethers and electron-deficient aromatic carbenium ions. In the absence of such inter-actions in (I) and (II), hydrogen bonding amongst the crown ethers, 4-carboxypyridinium cations and water molecules has the most obvious role in organizing the structures of the complexes. Sulfur-substituted pyridinium salts of 18-crown-6

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Figure 4
The packing of (II), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms which are not involved in hydrogen bonds have been omitted.

have been structurally characterized by Fonari *et al.* (2007). There is a similarity with this work in that the solvent water molecules again play important roles in binding neighbouring molecules into a corrugated chain. However, a difference is that the N atom of the pyridine ring in thionicotinamide has no connection with 18-crown-6, whilst the N atom of a thioamide group interacts with two crown ether O atoms, rather than the one interaction seen here.

Finally, this study is also relevant to our systematic investigation of dielectric, ferroelectric and phase-transition materials (Ye *et al.*, 2010; Zhang *et al.*, 2010), including organic compounds, metal–organic coordination compounds and organic–inorganic hybrids. The measurement of the dielectric constant of (I) as a function of temperature showed that the permittivity is basically temperature independent (dielectric constant of 2–4) below room temperature. Such a dielectric response suggests that this compound might not undergo a distinct structural phase transition in the lower-temperature range. Similarly, in the range from room temperature to near its melting point (m.p. > 470 K), the dielectric constant increases smoothly from 4 to 11 as a function of temperature, and no dielectric anomaly was observed.

Experimental

Isonicotinic acid (2 mmol, 0.246 g) and perchloric acid (75%, 2 mmol, 0.267 g) or tetrafluoroboric acid (50%, 2 mmol, 0.328 g) were dissolved in water (20 ml). An ethanol solution (20 ml) containing 18-crown-6 (2 mmol, 0.528 g) was then added to the solution. Single

crystals of (I) and (II) suitable for X-ray diffraction analysis were obtained *via* slow evaporation of the ethanol–water solution at room temperature over a period of two weeks. All crystals were colourless and of prismatic habit. **Caution!** Please note that perchlorate salts are shock sensitive and should be handled with care.

Compound (I)

Crystal data

$C_6H_6NO_2^+ \cdot ClO_4^- \cdot C_{12}H_{24}O_6 \cdot 2H_2O$	$V = 2582.7 (9)$ Å^3
$M_r = 523.91$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 14.668 (3)$ Å	$\mu = 0.21$ mm^{-1}
$b = 10.242 (2)$ Å	$T = 293$ K
$c = 17.191 (3)$ Å	$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury2 (2×2 bin mode) diffractometer	25360 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	5913 independent reflections
$T_{min} = 0.958$, $T_{max} = 0.958$	3940 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.148$	
$S = 1.03$	
5913 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
341 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
86 restraints	Absolute structure: Flack (1983), with 2856 Friedel pairs
	Flack parameter: −0.03 (8)

Compound (II)

Crystal data

$C_6H_6NO_2^+ \cdot BF_4^- \cdot C_{12}H_{24}O_6 \cdot 2H_2O$	$V = 2549.0 (9)$ Å^3
$M_r = 511.27$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 14.634 (3)$ Å	$\mu = 0.12$ mm^{-1}
$b = 10.177 (2)$ Å	$T = 293$ K
$c = 17.116 (3)$ Å	$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury2 (2×2 bin mode) diffractometer	25207 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	5828 independent reflections
$T_{min} = 0.976$, $T_{max} = 0.976$	3477 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.195$	
$S = 1.04$	
5828 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
342 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
86 restraints	Absolute structure: Flack (1983), with 2812 Friedel pairs
	Flack parameter: −0.1 (13)

Both the perchlorate and tetrafluoroborate anions were modelled as disordered over two sites. The site-occupancy factors of the majority component refined to 0.675 (4) and 0.656 (4) for (I) and (II), respectively. All bond lengths in the anions were restrained to reasonable distances [1.42 (1) and 1.38 (1) Å for Cl—O and B—F, respectively], and rigid-bond and similarity restraints were also applied to all atoms of the anions to ensure reasonable displacement

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O2^i	0.85 (2)	1.86 (2)	2.704 (4)	168 (4)
N1—H1$A\cdots$O1^i	0.85 (2)	2.51 (4)	2.916 (4)	110 (3)
O8—H8$C\cdots$O10^{ii}	0.84 (2)	1.70 (3)	2.510 (4)	159 (5)
O9—H9$D\cdots$O4	0.83 (2)	2.14 (2)	2.957 (4)	172 (6)
O9—H9$C\cdots$O6	0.84 (2)	2.08 (2)	2.913 (4)	169 (6)
O9—H9$C\cdots$O1	0.84 (2)	2.62 (5)	3.131 (4)	120 (5)
O10—H10$D\cdots$O9	0.84 (2)	1.86 (2)	2.699 (4)	171 (5)
O10—H10$C\cdots$O12^{iii}	0.85 (2)	1.96 (3)	2.762 (8)	155 (5)
O10—H10$C\cdots$O12A^{iii}	0.85 (2)	2.05 (3)	2.901 (17)	176 (5)
O10—H10$C\cdots$O13A^{iii}	0.85 (2)	2.64 (5)	3.146 (13)	119 (4)
O10—H10$C\cdots$Cl1^{iii}	0.85 (2)	2.85 (3)	3.616 (7)	151 (5)
O10—H10$C\cdots$Cl1A^{iii}	0.85 (2)	2.86 (4)	3.618 (14)	149 (5)

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O8—H8$C\cdots$O9^i	0.84 (2)	1.69 (3)	2.514 (4)	164 (6)
O9—H9$C\cdots$F2	0.84 (2)	1.89 (2)	2.724 (8)	173 (7)
O9—H9$C\cdots$F2A	0.84 (2)	2.11 (4)	2.871 (15)	151 (6)
O9—H9$C\cdots$F1A	0.84 (2)	2.45 (5)	3.046 (13)	128 (5)
O9—H9$D\cdots$O10^{ii}	0.85 (2)	1.86 (2)	2.695 (5)	165 (6)
O10—H10$C\cdots$O3^{iii}	0.86 (2)	2.09 (2)	2.945 (4)	170 (6)
O10—H10$D\cdots$O1^{iii}	0.87 (2)	2.15 (4)	2.924 (4)	148 (6)
O10—H10$D\cdots$O6^{iii}	0.87 (2)	2.46 (4)	3.145 (5)	137 (5)
N1—H1$C\cdots$O5	0.87 (2)	1.86 (2)	2.711 (4)	170 (4)

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

parameters were obtained. Constraints were added to give equivalent displacement parameters for the corresponding atoms of the minor and major disorder components. Rigid-bond restraints were also applied to the displacement parameters of atoms C1 and C2 in (I), and C5 and C6 in (II). As the absolute structure could not be determined reliably in the absence of significant anomalously scattering atoms, the direction of the polar axis was chosen arbitrarily.

All H atoms bound to C atoms were placed in calculated positions and refined in riding mode, with C—H = 0.93 and 0.97 Å for aromatic and methylene C atoms, respectively, and with U_{iso}(H) = 1.2U_{eq}(C). All the N- and O-bound H atoms were discernible in the difference electron-density maps. These atoms were placed as found and

allowed to refine with the O—H distances restrained to 0.85 (2) Å, and the N—H distances restrained to 0.86 (2) and 0.87 (2) Å in (I) and (II), respectively. Additionally, H$\cdots$H distance restraints of 1.33 (3) and 1.40 (3) Å were applied for the water molecules in (I) and (II), respectively. For water H atoms, U_{iso}(H) = 1.5U_{eq}(O), and for others U_{iso}(H) = 1.2U_{eq}(parent). In total, each structure had 86 restraints imposed.

For both compounds, 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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