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Hydrogen-bonding motifs in 4-carboxyphenylammonium nitrate and perchlorate monohydrate, and in bis(4-carboxyphenylammonium) sulfate

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In the title compounds, $C_7H_8NO_2^+\cdot NO_3^-$, (I), $C_7H_8NO_2^+\cdot ClO_4^-\cdot H_2O$, (II), and $2C_7H_8NO_2^+\cdot SO_4^{2-}$, (III), the carboxyl planes of the 4-carboxyphenylammonium cations are twisted from the aromatic plane. A homonuclear $C(8)$ hydrogen-bonding motif of 4-carboxyphenylammonium cations is observed in both (I) and (II), leading to 'head-to-tail' layers. The cations in (III) form carboxyl group dimers, making a graph-set motif of $R_2^2(8)$. In all the structures, anions connect the cationic layers and an infinite chain running along the c axis is observed, having the $C_2^2(6)$ graph-set motif. Interestingly, in (II), the anions are connected through weak hydrogen bonds involving the water molecules, leading to a graph-set motif of $R_4^4(12)$. Alternate hydrophobic and hydrophilic layers are observed in all three compounds as a result of the column-like arrangement of the aromatic rings of the cations and the anions. Furthermore, in (I), head-to-tail N—H···O interactions and interactions linking the cations and anions form an $R_6^4(16)$ hydrogen-bonding motif, resulting in a pseudo-inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$.

Comment

4-Aminobenzoic acid (PABA) is an essential biological molecule, acting as a bacterial cofactor involved in the synthesis of folic acid. PABA is also a starting material in the manufacture of target esters, salts, folic acid, azo dyes and some other organic compounds. It is used in medicine for preparing local anesthetics and ointments. PABA has proved to be a versatile reagent for structure extension by linear hydrogen-bonding associations, through both the carboxylic acid and the amine functional groups. Considering these facts and to study the hydrogen-bonding association by different graph-set motifs, PABA was treated with three different inorganic acids, *viz.* nitric acid, perchloric acid and sulfuric acid, and crystals of 4-carboxyphenylammonium nitrate, (I), 4-carboxyphenylammonium perchlorate monohydrate, (II), and bis(4-car-

boxyphenylammonium) sulfate, (III), were obtained. As expected, PABA forms protonated units with the transfer of a H atom from the inorganic acid; correspondingly, the crystal is stabilized by an extensive intermolecular hydrogen-bonding network. Crystallographic studies of PABA compounds were initiated by Pant (1965), who studied the crystal structure of 3,5-dibromo-4-aminobenzoic acid. Later, Lai & Marsh (1967) extensively studied the structure of this vitamin. The structures of 4-carboxyanilinium dihydrogenmonoarsenate monohydrate (Tordjman *et al.*, 1988), 2,4,6-trinitrobenzoic acid 4-aminobenzoic acid monohydrate (Lynch *et al.*, 1992), bis(4-aminobenzoic acid)dichlorocadmium(II) (Le Fur & Masse, 1996), 4-carboxyanilinium (2*R*,3*R*)-hydrogen tartrate monohydrate (Hu *et al.*, 2002) and bis(4-aminobenzoic acid)-silver(I) nitrate (Wang *et al.*, 2004) have been reported previously.
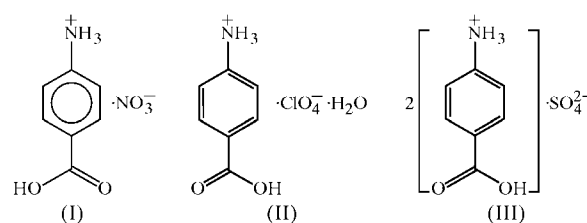
The asymmetric part of (I) contains two planar units, namely, a 4-carboxyphenylammonium cation and a nitrate anion, nearly perpendicular to one another, with a dihedral angle of 85.9 (8)° (Fig. 1). 4-Carboxyphenylammonium cations are stacked almost parallel to the (001) plane, the small
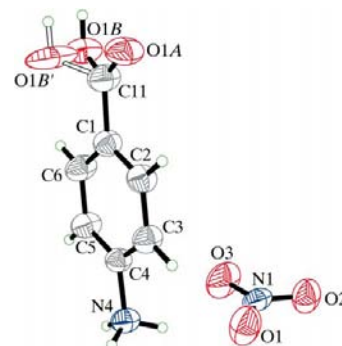

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The major (75%) and minor (25%) occupancies of the hydroxy group are shown.
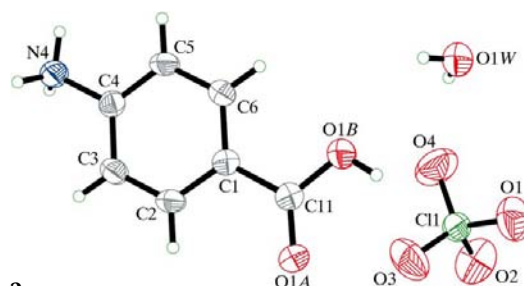

Figure 2
The molecular structure of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

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angular deviation of this plane being only 3.89 (2)°. In (II), the asymmetric part of the unit cell contains a 4-caboxyphenyl-ammonium cation, a perchlorate anion and a solvent water
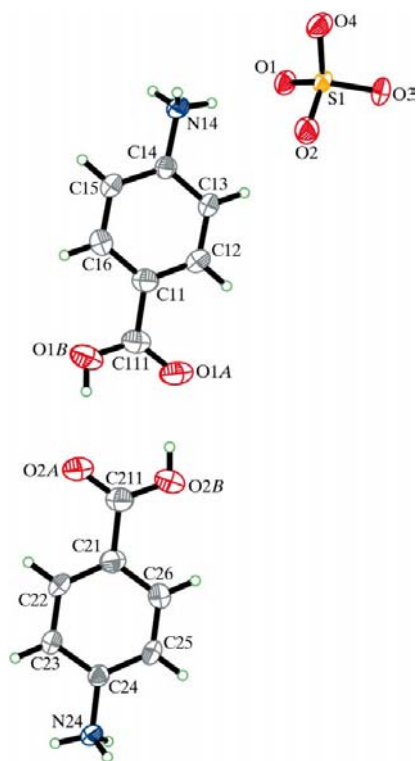

Figure 3
The molecular structure of (III), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

molecule (Fig. 2). Two crystallographically independent 4-carboxyphenylammonium cations and a sulfate anion constitute the asymmetric part of (III) (Fig. 3). In all three compounds, the transfer of a proton from the inorganic acid leads to protonation on the NH_2 site of the bacterial vitamin PABA and forms the 4-carboxyphenylammonium (or 4-carboxyanilinium) cation. The protonation on the cation (NH_3^+) is confirmed by comparison of the C—N bond distances (Tables 1, 3 and 5) with the literature value of 1.38 Å for the unprotonated NH_2 group (Lai & Marsh, 1967).

In (I) and (II), the heads (NH_3^+) and tails (COOH) of the cations are connected through glide-related hydrogen bonds [N4—H4A···O1A($-x + 2$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$) and N4—H4A···O1A($x - 1$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$), respectively], leading to a $C(8)$ hydrogen-bonding graph-set motif. In (I), these motifs form a layered structure stacked parallel to the ab plane with an inter-layer distance of 6.695 (7) Å. In (II), aggregation of these $C(8)$ motifs leads to a sheet-like structure on the ($\overline{1}02$) parallel planes of the unit cell, resulting in strong X-ray reflections for the corresponding planes. These sheets are stacked with an inter-layer distance of 7.009 (5) Å. From the Cambridge Structural Database (Allen, 2002), it is observed that a head-to-tail hydrogen-bonding association and carboxylic group dimerization are characteristic features found in most PABA complexes. The former feature is observed in (I) and (II), and the latter in (III). In (III), the carboxyl groups of the cations are dimerized through O1B—H1B···O2A and O2B···H2B···O1A hydrogen bonds, leading to a graph-set motif of $R_2^2(8)$. Schematic diagrams of the different hydrogen-bond motifs are shown in Fig. 4.
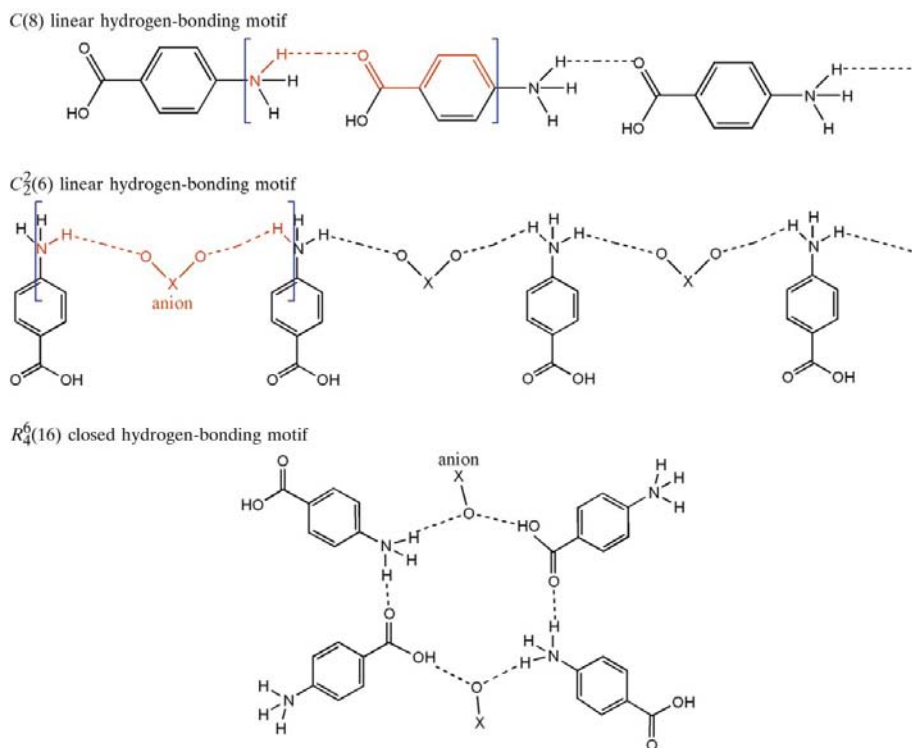

Figure 4
Schemes showing the different hydrogen-bonding motifs.

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In all three structures, twisting of the carboxyl plane from the aromatic ring is observed. The twist angles are 9.55 (9)° in (I), 6.25 (3)° in (II), and 5.95 (3) and 3.41 (2)° for the two cations in (III). In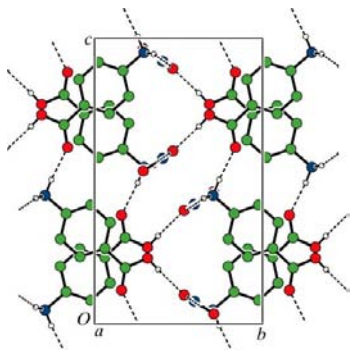 (II), atom O1A deviates by 0.151 (4) Å, which is more than the deviation of O1B (the hydroxy atom), whereas in (I) and both the residues of (III), atom O1B deviates [0.277 (7) Å in (I), and 0.215 (7) and 0.121 (6) Å in (III)] more than O1A. This twisting of the carboxyl group is due to the hydrogen-bonding association and the packing specificity of the crystal. In all three structures, the cations are linked by the anions through N—H···O bonds to form an infinite chain running along the c axis, with the linear $C_2^2(6)$ graph-set motif [N4—H4C···O1/N4—H4B···O2(x, y, z + 1) in (I), N4—H4B···O2(x − 1, −y + ½, z + ½)/N4—H4C··· O3(x − 1, −y + ½, z − ½) in (II), and N14—H14B··· O2(x, y, z − 1)/N14—H14C···O1 and N24—H24A··· O4(x + 1, y, z + 1)/N24—H24C···O3(x + 1, y, z) in the cations of (III)].

Figure 5
The packing of (I), viewed down the a axis. Hydrogen bonds are drawn as dashed lines and H atoms not involved in these interactions have been omitted.
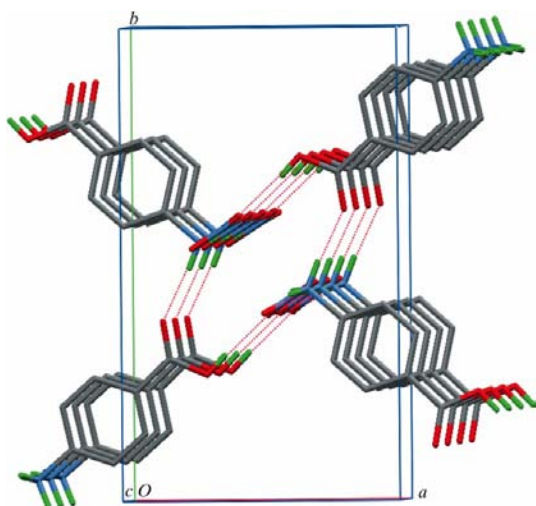

Figure 6
The pseudo-inversion centre and the cavity formed by anions and cations in the $R_6^4(16)$ hydrogen-bonded motif in (I). Hydrogen bonds are drawn as dotted lines and C-bound H atoms have been omitted.
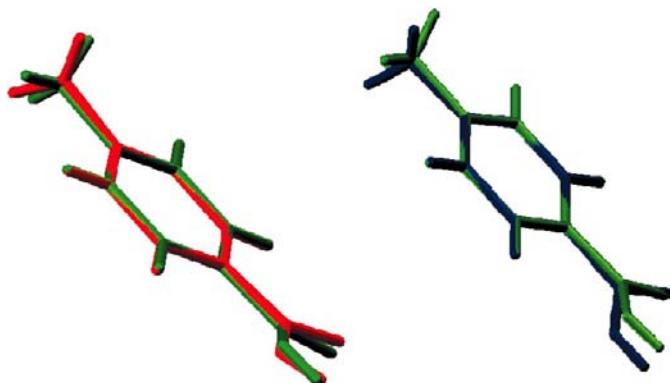

Figure 7
Structural overlay diagram of 4-carboxyphenylammonium cations in (I) and (III) [the minor occupancy component of the OH group in (I) has been omitted].

Figure 8
The packing of (II), viewed down the a axis. Hydrogen bonds are drawn as dashed lines and H atoms not involved in these interactions have been omitted.

Figure 9
Head-to-tail C(8) and linear $C_2^2(6)$ hydrogen-bonding motifs, resulting in a secondary structure of an $R_3^3(28)$ motif in (II). Hydrogen bonds are drawn as dotted lines.

Figure 10
The $R_4^4(12)$ hydrogen-bonding motif formed by the interaction between perchlorate and water molecules in (II). Hydrogen bonds are drawn as dotted lines.

The packing diagram of (I) in Fig. 5 shows hydrophobic layers formed by the stacking of aromatic rings at $x = 0$. Also in (I), a hydrogen-bonding graph-set motif of $R_6^4(16)$ exists as a result of glide-related direct interactions, and interactions involving the anions and the amine and carboxyl groups. These closed rings of size 2.850×8.681 Å (including contact radii) extend along the c axis. This closed-ring $R_6^4(16)$ structure results in a pseudo-inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$, which is extended as a pseudo-inversion axis through $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 6). Such pseudosymmetries are also observed in the structure of PABA (Lai & Marsh, 1967). Fig. 7 represents the structural overlay of the cation in (I) (the minor occupancy component of the OH group has been omitted) with both the residues of (III) by fitting the atoms of the aromatic ring. A slight deviation of the amino and carboxyl groups of the cations in (I) is observed.

In (II), perchlorate anions are sandwiched between hydrophobic layers of cations at $y = \frac{1}{4}$ and $\frac{3}{4}$, thus forming alternating hydrophilic and hydrophobic columns in the bc plane of the unit cell (Fig. 8). Primary $C_2^2(6)$ graph-set motifs

connect two adjacent sheets of 4-carboxyphenylammonium ions formed by the above-mentioned $C(8)$ primary graph-set motif. Combination of these two primary motifs leads to a new secondary graph-set motif $R_6^6(28)$ (Fig. 9). The water molecules interact with the anions through weak hydrogen bonds, connecting two inversely related perchlorate anions to form a closed hydrogen-bonding dimer or ring, leading to a graph-set motif of $R_4^4(12)$ (Fig. 10). These motifs are connected linearly along the c axis by another weak interaction [O1$W\cdots$ O4$(-x + 1, -y + 1, -z + 1) = 3.162$ (4) Å]. Three-centred hydrogen bonds, formed by the amino group with the anion, relate two inversely related cations through weak hydrogen bonds [N4—H4$C\cdots$O1$(x - 1, -y + \frac{1}{2}, z + \frac{1}{2})$ and N4—H4$C\cdots$O3$(-x + 1, y + \frac{1}{2}, -z + \frac{3}{2})$], resulting in a graph-set motif of $R_2^4(10)$.

In (III), the sulfate anions are stacked nearly at $x = 0$, forming hydrophilic columns. Alternatively, hydrophobic layers are observed nearly at $x = \frac{1}{2}$ and $\frac{3}{4}$ owing to the stacking of aromatic rings (Fig. 11). The anions are connected to the cationic dimers through extensive hydrogen bonding between the O atoms of the anion and the amino group. The cationic dimers connected by the above-mentioned $C_2^2(6)$ hydrogen-bond motifs form a sheet-like structure parallel to the ac plane (Fig. 12). The planes of the cationic dimers make a dihedral angle of 20.87° with the ac plane of the unit cell.
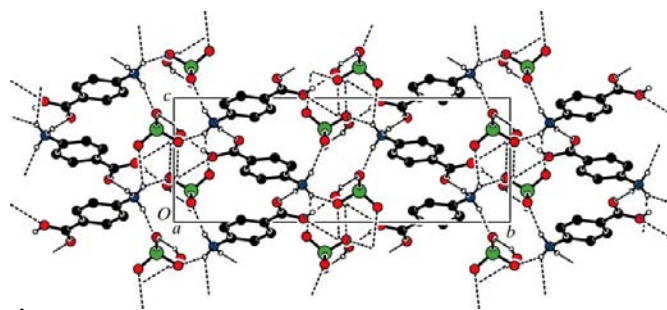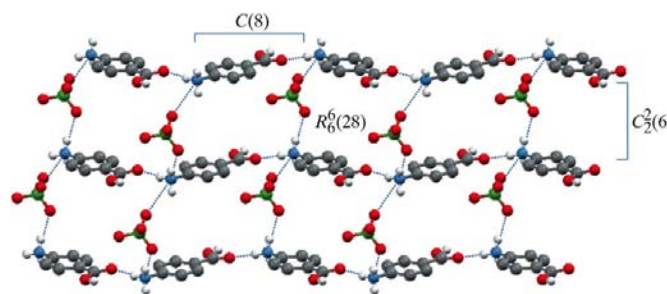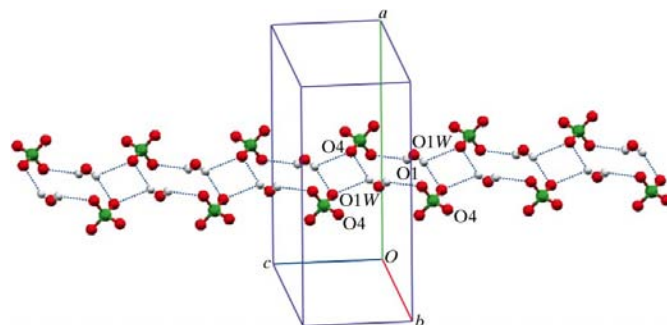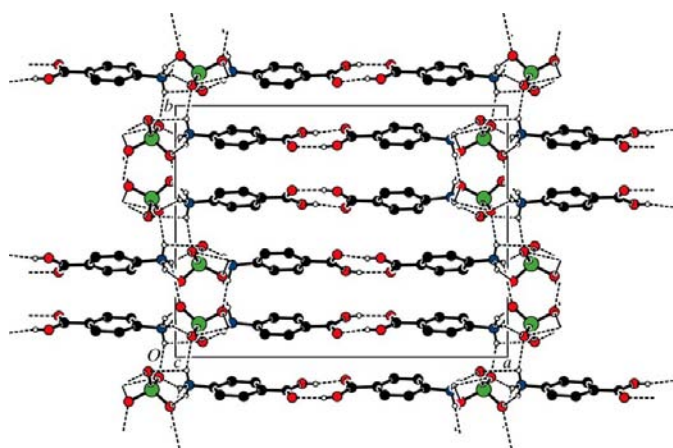

Figure 11
The packing of (III), viewed down the c axis. Hydrogen bonds are drawn as dashed lines and H atoms not involved in these interactions have been omitted.
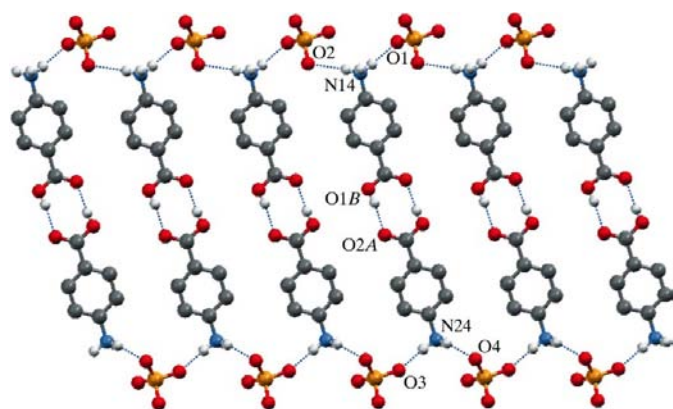

Figure 12
Molecular aggregation of cationic dimers [$R_2^2(6)$ motif] and the $C_2^2(6)$ graph-set motif running along the c axis, forming a sheet-like structure in (III). Hydrogen bonds are drawn as dotted lines and C-bound H atoms have been omitted.

Experimental

The title compounds, (I)–(III), were crystallized at room temperature by slow evaporation from aqueous solutions containing 4-aminobenzoic acid with nitric acid, perchloric acid and sulfuric acid in the stoichiometric ratios 1:1, 1:1 and 1:2, respectively.

Compound (I)

Crystal data

$C_7H_8NO_2^+\cdot NO_3^-$	$D_m = 1.49$ Mg m^{-3}
$M_r = 200.15$	D_m measured by flotation using a
Monoclinic, $P2_1/c$	liquid mixture of xylene and
$a = 8.8154$ (9) Å	bromoform
$b = 15.0516$ (3) Å	Mo $K\alpha$ radiation
$c = 6.6950$ (6) Å	$\mu = 0.13$ mm^{-1}
$\beta = 90.933$ (12)°	$T = 293$ (2) K
$V = 888.14$ (14) Å^3	Block, light pink
$Z = 4$	$0.22 \times 0.19 \times 0.17$ mm
$D_x = 1.497$ Mg m^{-3}	

Data collection

Nonius MACH3 sealed-tube	$R_{int} = 0.016$
diffractometer	$\theta_{max} = 25.0°$
ω–2θ scans	3 standard reflections
1832 measured reflections	frequency: 60 min
1549 independent reflections	intensity decay: none
1264 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 0.3551P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
1549 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
139 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.047 (6)

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Table 1
Selected geometric parameters (Å, °) for (I).

C4—N4	1.468 (2)	C11—O1B	1.333 (3)
C11—O1A	1.211 (3)		
O1A—C11—C1	123.1 (2)	O1B—C11—C1	113.2 (2)
C2—C1—C11—O1A	−7.9 (3)	C6—C1—C11—O1B	−13.0 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1B—H1$B\cdots$O1^i	0.82	2.57	3.202 (3)	135
O1B'—H1$B'\cdots$O2^i	0.82	2.32	3.038 (10)	146
N4—H4$A\cdots$O1A^{ii}	0.89	1.91	2.791 (2)	171
N4—H4$B\cdots$O2^{iii}	0.89	1.99	2.853 (2)	163
N4—H4$C\cdots$O1	0.89	1.98	2.852 (3)	167

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

Compound (II)

Crystal data

$C_7H_8NO_2^+\cdot ClO_4^-\cdot H_2O$	$D_m = 1.61$ Mg m^{-3}
$M_r = 255.61$	D_m measured by flotation using a
Monoclinic, $P2_1/c$	liquid mixture of carbon tetra-
$a = 7.5492$ (7) Å	chloride and bromoform
$b = 19.3871$ (5) Å	Mo $K\alpha$ radiation
$c = 7.2974$ (3) Å	$\mu = 0.39$ mm^{-1}
$\beta = 101.524$ (5)°	$T = 293$ (2) K
$V = 1046.42$ (12) Å^3	Block, light pink
$Z = 4$	$0.23 \times 0.20 \times 0.18$ mm
$D_x = 1.622$ Mg m^{-3}	

Data collection

Nonius MACH3 sealed-tube diffractometer	1833 independent reflections
ω–2θ scans	1587 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.029$
$T_{min} = 0.911$, $T_{max} = 0.994$ (expected range = 0.854–0.933)	$\theta_{max} = 25.0°$
	3 standard reflections
	frequency: 60 min
3032 measured reflections	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.8272P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1833 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.049 (4)

Table 3
Selected geometric parameters (Å, °) for (II).

C4—N4	1.466 (3)	C11—O1B	1.317 (3)
C11—O1A	1.211 (3)		
C2—C1—C11—O1A	−5.8 (4)	C6—C1—C11—O1B	−6.1 (3)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$A\cdots$O1A^i	0.89	1.93	2.818 (3)	173
N4—H4$B\cdots$O2^{ii}	0.89	2.04	2.906 (3)	164
N4—H4$C\cdots$O1^{iii}	0.89	2.22	3.018 (3)	150
O1B—H1$B\cdots$O1W^{iv}	0.82	1.83	2.641 (3)	171
O1W—H1$W\cdots$O4	0.794 (19)	2.39 (3)	3.116 (4)	152 (4)
O1W—H2$W\cdots$O1^{iv}	0.81 (2)	2.47 (4)	3.096 (4)	135 (4)

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

Compound (III)

Crystal data

$2C_7H_8NO_2^+\cdot SO_4^{2-}$	$D_m = 1.56$ Mg m^{-3}
$M_r = 372.35$	D_m measured by flotation using a
Monoclinic, $P2_1/c$	liquid mixture of carbon xylene
$a = 18.7094$ (8) Å	and bromoform
$b = 14.0562$ (4) Å	Mo $K\alpha$ radiation
$c = 6.0551$ (5) Å	$\mu = 0.25$ mm^{-1}
$\beta = 97.272$ (5)°	$T = 293$ (2) K
$V = 1579.51$ (15) Å^3	Block, light pink
$Z = 4$	$0.26 \times 0.22 \times 0.18$ mm
$D_x = 1.566$ Mg m^{-3}	

Data collection

Nonius MACH3 sealed-tube diffractometer	2763 independent reflections
ω–2θ scans	2014 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.045$
$T_{min} = 0.953$, $T_{max} = 0.997$	$\theta_{max} = 25.0°$
	3 standard reflections
	frequency: 60 min
3323 measured reflections	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1287P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$+ 0.1992P]$
$wR(F^2) = 0.181$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2763 reflections	$\Delta\rho_{max} = 0.84$ e Å^{-3}
230 parameters	$\Delta\rho_{min} = -0.69$ e Å^{-3}
H-atom parameters constrained	

Table 5
Selected geometric parameters (Å, °) for (III).

C111—O1A	1.241 (5)	C211—O2A	1.237 (5)
C111—O1B	1.268 (5)	C211—O2B	1.276 (5)
C14—N14	1.452 (4)	C24—N24	1.447 (4)
C12—C11—C111—O1A	−1.8 (6)	C22—C21—C211—O2A	2.1 (6)
C16—C11—C111—O1A	−179.6 (4)	C26—C21—C211—O2A	−179.6 (4)

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1B—H1$B\cdots$O2A	0.82	1.86	2.670 (4)	170
N14—H14$A\cdots$O2^i	0.89	1.79	2.682 (3)	175
N14—H14$B\cdots$O2^{ii}	0.89	2.22	2.936 (3)	137
N14—H14$C\cdots$O1	0.89	1.89	2.757 (3)	165
O2B—H2$B\cdots$O1A	0.82	1.80	2.614 (4)	171
N24—H24$A\cdots$O4^{iii}	0.89	1.97	2.804 (3)	156
N24—H24$B\cdots$O3^{iv}	0.89	1.93	2.741 (3)	151
N24—H24$C\cdots$O3^v	0.89	1.94	2.752 (3)	150

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

The water H atoms in (II) were located and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, O—H = 0.82 Å and N—H = 0.89 Å, and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). In (I), the O1B hydroxy group is disordered over two positions, with major and minor site occupancies of 0.75 and 0.25, respectively.

For all compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*, *MERCURY* (Version 1.4.1; Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3034). Services for accessing these data are described at the back of the journal.

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