

Hydrogen bonding in the inner-salt zwitterion and in two different charged forms of 5,6-bis(2-pyridyl)-pyrazine-2,3-dicarboxylic acid

Montserrat Alfonso, Yi Wang and Helen Stoeckli-Evans*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case Postale 2, CH-2007 Neuchâtel, Switzerland

Correspondence e-mail: helen.stoeckli-evans@unine.ch

Received 15 May 2001

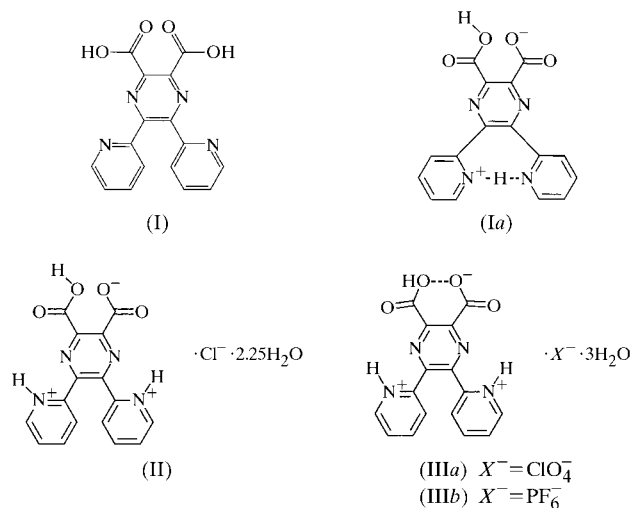
Accepted 27 June 2001

5,6-Bis(2-pyridyl)pyrazine-2,3-dicarboxylic acid exists as an inner-salt zwitterion, 3-carboxy-5-(2-pyridinio)-6-(2-pyridyl)pyrazine-2-carboxylate, (*Ia*), $C_{16}H_{10}N_4O_4$. The adjacent pyridine and pyridinium rings are almost coplanar due to the presence of an intramolecular hydrogen bond involving the pyridine N atom and the NH H atom of the pyridinium group. In the crystal of (*Ia*), symmetry-related molecules are hydrogen bonded *via* the carboxylic acid OH group and one of the carboxylate O atoms to form a polymer, which exhibits a channel-type structure. In the HCl, HClO₄ and HPF₆ salts, 6-carboxy-5-carboxylatopyrazine-2,3-diyl-di-2-pyridinium chloride 2.25-hydrate, (*II*), $C_{16}H_{11}N_4O_4^+ \cdot Cl^- \cdot 2.25H_2O$, 6-carboxy-5-carboxylatopyrazine-2,3-diyl-di-2-pyridinium perchlorate trihydrate, (*IIIa*), $C_{16}H_{11}N_4O_4^+ \cdot ClO_4^- \cdot 3H_2O$, and 6-carboxy-5-carboxylatopyrazine-2,3-diyl-di-2-pyridinium hexafluorophosphate trihydrate, (*IIIb*), $C_{16}H_{11}N_4O_4^+ \cdot PF_6^- \cdot 3H_2O$, both pyridine rings are protonated. In the perchlorate form, and in the isomorphous hexafluorophosphate form, the molecule possesses *C*₂ symmetry, with has a symmetrical intramolecular hydrogen bond involving the adjacent carboxylate and carboxylic acid substituents. In the crystals of the chloride and perchlorate (or hexafluorophosphate) salts, hydrogen-bonded polymers are formed which are three-dimensional and one-dimensional, respectively.

Comment

The potentially bis-tridentate coordinating ligand 5,6-bis(2-pyridyl)pyrazine-2,3-dicarboxylic acid, (*I*), was synthesized in order to study its coordination behaviour with transition metals, and it does indeed exhibit a highly diverse coordination geometry. At least eight different coordination modes have been observed in the formation of mononuclear, binuclear and polymeric coordination complexes (Alfonso *et al.*, 2001). A prominent characteristic of this compound is its amphoteric character. It can exist as an inner-salt zwitterion, (*Ia*), and as different charged species, for example, as in the

chloride 2.25-hydrate, (*II*), or the perchlorate and hexafluorophosphate trihydrate salts, (*IIIa*) and (*IIIb*), as shown in the Scheme below.



When recrystallized from water, compound (*I*) exists as the inner-salt zwitterion, (*Ia*) (Fig. 1). As a result of an intramolecular hydrogen bond involving the pyridinium N⁺—H and the pyridine N atoms, the adjacent pyridine (py) rings are almost coplanar with the central pyrazine (pz) ring, with a pyH-to-pz dihedral angle of 4.3 (1)° and a py-to-pz dihedral angle of 7.9 (1)°. The N atoms are separated by 2.528 (3) Å, and this rather short intramolecular hydrogen bond [N3—H3 1.22 (3) and H3···N4 1.32 (3) Å, and N3—H3···N4 167 (3)°; Table 1] leads to a slight twist of the pyrazine ring (plane C1/N1/C4 to plane C2/N2/C3) of 3.6 (4)°, as well as to two unusually large exocyclic angles, C3—C4—C5 [131.0 (3)°] and C4—C3—C10 [131.2 (2)°]. This type of hydrogen bond, with almost identical bond distances and angles, was also found in

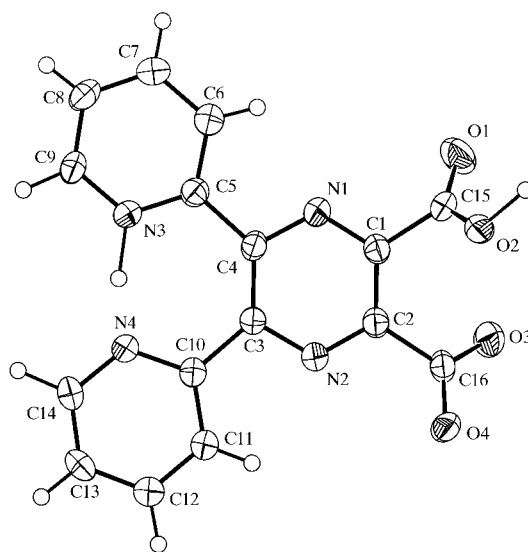


Figure 1
The molecular structure of (*Ia*) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

the diprotonated form of tetra(2-pyridyl)pyrazine by Bock *et al.* (1992) and analysed theoretically. An analysis of hydrogen bonding in organoammonium H(N) atoms of this type has been made by Robertson *et al.* (1998).

The carboxylate group (C16/O3/O4) and the carboxylic acid group (C15/O1/O2) are rotated out of the plane of the pyrazine ring. They are inclined to one another by $59.5(3)^\circ$, and to the pyrazine ring by $37.9(1)$ and $58.3(2)^\circ$, respectively. In the crystal of (Ia), symmetry-related molecules are hydrogen bonded *via* the carboxylic acid OH group and one of the carboxylate O atoms (Table 1). This results in the formation of a one-dimensional polymer with a channel-type structure (Fig. 2). A similar strong intermolecular O—H...O hydrogen bond, with almost identical bond distances and angles, has been observed previously in caesium trihydrogen diphthalate (Krol *et al.*, 1983).

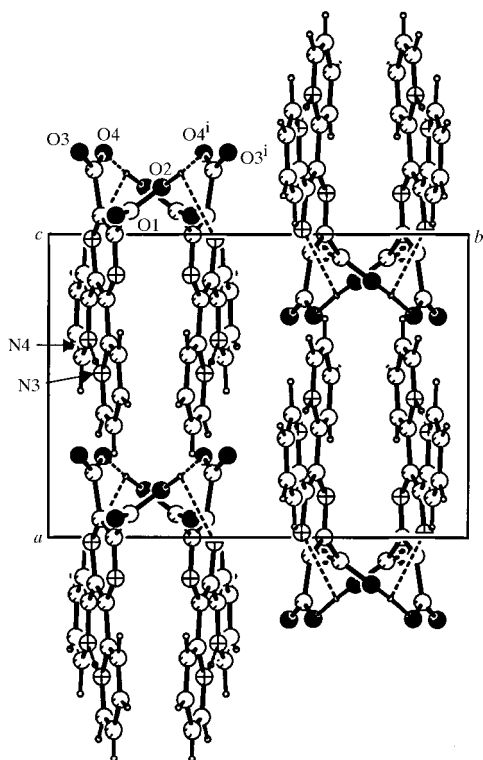


Figure 2
The crystal packing of (Ia) viewed down the *c* axis. The hydrogen bonding is shown as dashed lines (the symmetry code is as in Table 1).

Recrystallization of (Ia) from 1 M HCl yielded colourless single crystals of (II) (Fig. 3). Here, both of the pyridine rings are protonated and they are both rotated by *ca* 180° from their positions in (Ia). They are inclined to one another by $65.6(1)^\circ$, and by $49.2(1)$ (N3/C5–C9) and $30.8(1)^\circ$ (N4/C10–C14) to the pyrazine ring. This places the pyridine N atoms slightly above and below the plane of the pyrazine ring, which is twisted by $4.9(2)^\circ$ (plane C1/N1/C4 to plane C2/N2/C3). The carboxylic acid group (C15/O1/O2) is out of the plane of the pyrazine ring by $75.7(1)^\circ$, compared with $58.3(1)^\circ$ in (Ia). The carboxylate group (C16/O3/O4) is inclined to the pyrazine ring by only $15.3(3)^\circ$, compared with $37.9(1)^\circ$ in (Ia).

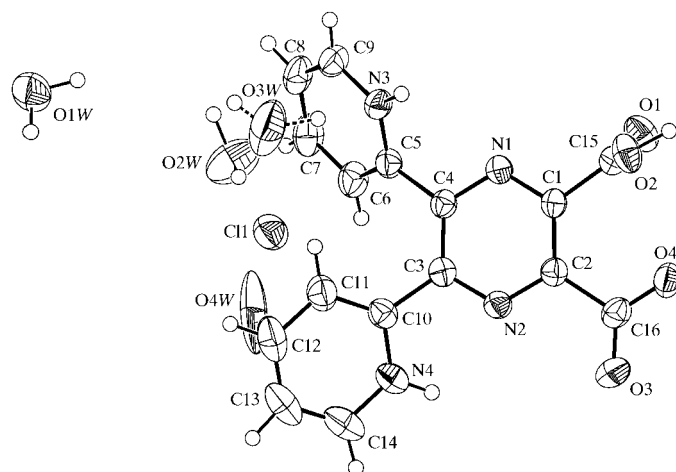


Figure 3
The molecular structure of (II) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

This triprotonated form, (II), also differs from (Ia) in the type of hydrogen bonding. There are no intramolecular hydrogen bonds in the crystal structure of (II). However, symmetry-related molecules are linked by hydrogen bonds to form a three-dimensional hydrogen-bonded network. This involves the N atoms of both protonated pyridine rings, the O atoms of the carboxylate, the OH group of the carboxylic acid, the lattice water molecules and the Cl^- anion, which participates in four hydrogen-bond interactions; details are given in Table 2 and Fig. 4.

A second triprotonated form, (IIIa), was obtained on slow evaporation of a solution of (Ia) in 1 M HClO_4 . Compound (IIIa) possesses C_2 symmetry and its structure differs signifi-

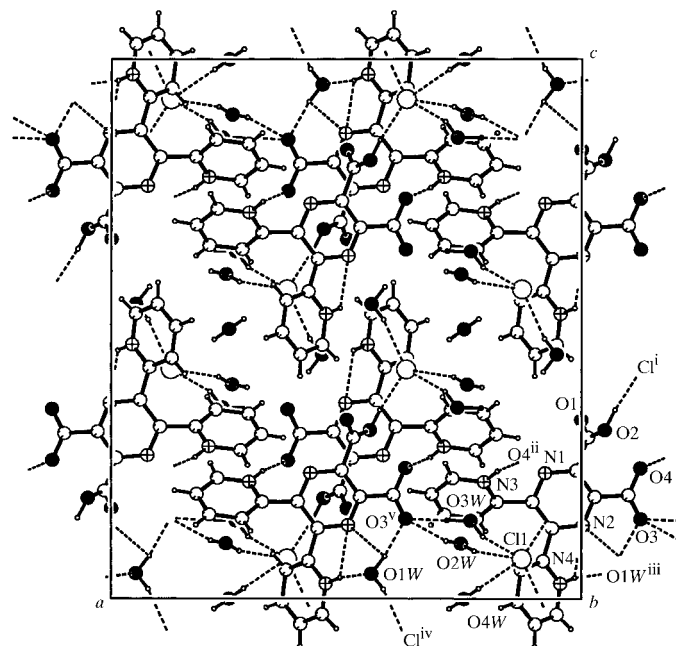


Figure 4
The crystal packing of (II) viewed down the *b* axis. The hydrogen bonding is shown as dashed lines (the symmetry codes are as in Table 2).

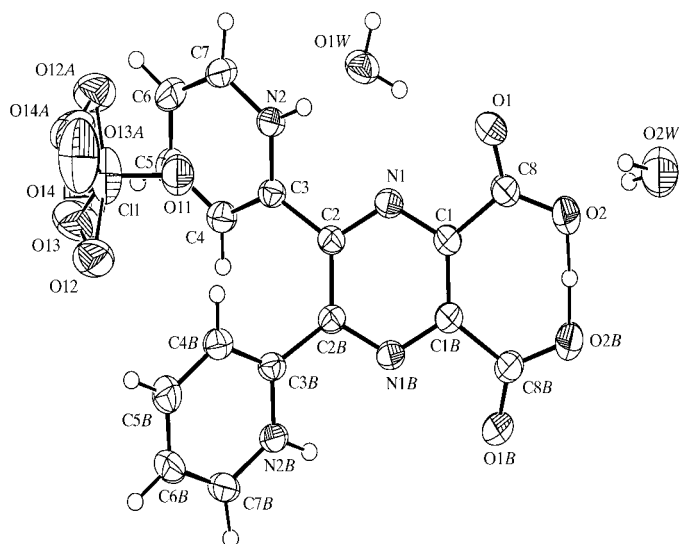


Figure 5
The molecular structure of (IIIa) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

cantly from that of (Ia) (Fig. 5). Here again, both pyridine rings are protonated and are twisted out of the plane of the pyrazine ring by $34.8(1)^\circ$, and inclined to one another by $62.2(1)^\circ$. The carboxylate and carboxylic acid groups are both inclined to the pyrazine plane by $19.7(3)^\circ$ and to one another by $5.2(4)^\circ$. This arrangement is the result of the presence of a strong symmetrical intramolecular hydrogen bond (Table 3). This type of symmetrical hydrogen bond has been observed previously in pyrazine-2,3-dicarboxylic acid 3-amino-1,2,4-triazole (Lynch *et al.*, 1994) and in bis[dihydrogen 1,2,4,5-benzenetetracarboxylate(2-)] (Karanović *et al.*, 1999). It is interesting to note that the deviation from planarity of the pyrazine ring is larger than in (Ia) or (II), with a twist angle of $9.6(4)^\circ$. In the crystal, the $C_{16}H_{11}N_4O_4^+$ cations and the lattice

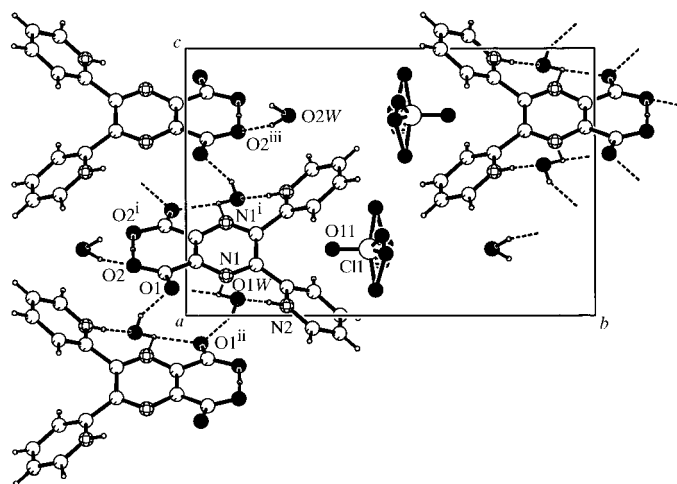


Figure 6
Part of the crystal packing of (IIIa) viewed down the *a* axis. The hydrogen bonding, which extends in both the *a* and *c* directions, is shown as dashed lines (the symmetry codes are as in Table 3).

water form a one-dimensional hydrogen-bonded polymer, separated by the disordered perchlorate anions; details are given in Table 3 and Fig. 6.

On reaction of (Ia) with $Ag[PF_6]$ in water, a silver complex was not obtained, but slow evaporation of the solution gave crystals of (IIIb) (Fig. 7), which proved to be isomorphous with (IIIa). The structural details for (IIIb) are very similar to those observed for (IIIa). Details concerning the hydrogen bonding are given in Table 4 and Fig. 8.

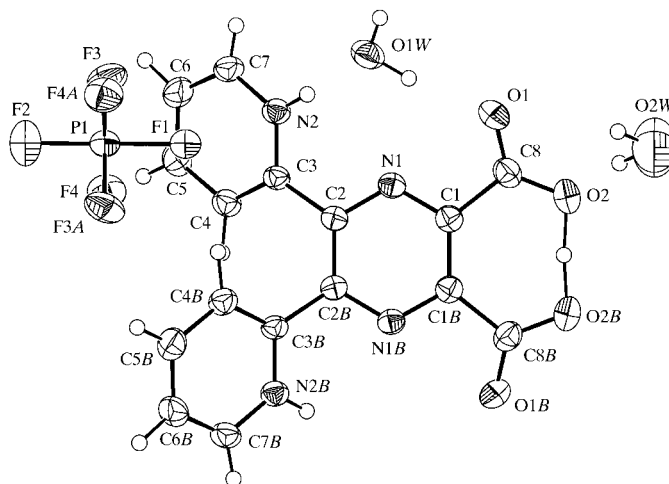


Figure 7
The molecular structure of (IIIb) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

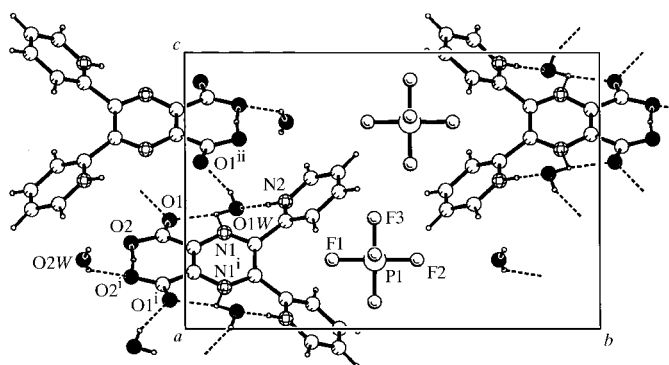


Figure 8
Part of the crystal packing of (IIIb) viewed down the *a* axis. The hydrogen bonding, which extends in both the *a* and *c* directions, is shown as dashed lines (the symmetry codes are as in Table 4).

Experimental

Compound (Ia) was prepared by adding 2,3-bis(2-pyridyl)-quinoxaline (5.7 g, 20 mmol; Goodwin & Lions, 1959) to water (450 ml). This solution was heated to 368 K with stirring. $KMnO_4$ (25 g, 0.16 mol) was then added in small portions over a period of 2 h. The reaction mixture was stirred for 1 h and the temperature reduced

to 348 K. Ethanol (10 ml) was added to remove the excess KMnO_4 . The reaction mixture was filtered to give a colourless filtrate, which was concentrated to 20 ml and acidified with 4 M HCl until a white precipitate formed. The crude product was dissolved in water (15 ml) and the solution was acidified again with concentrated HCl to yield a white solid. The product, (Ia), was filtered off, washed with ethanol, recrystallized from water and dried under vacuum (yield 3.9 g, 60.5%; m.p. 533–534 K). Analysis calculated for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4$: C 59.6, H 3.1, N 17.4%; found: C 59.5, H 3.0, N 17.3%. Selected IR bands (KBr , cm^{-1}): 3426 (*br, m*), 3083 (*w*), 3026 (*w*), 2922 (*w*), 2854 (*w*), 1706 (*m*), 1653 (*m*), 1602 (*vs*), 1488 (*s*), 1433 (*m*), 1337 (*m*), 1268 (*s*), 1148 (*s*), 1115 (*s*), 1083 (*s*), 1040 (*m*), 943 (*m*), 865 (*m*), 820 (*w*), 793 (*vs*), 743 (*s*); ^1H NMR (D_2O , 200 MHz, δ , p.p.m.): 8.84–8.82 (*m*, 2H, PyH), 8.46–8.37 (*m*, 2H, PyH), 8.08–7.99 (*m*, 4H, PyH); ^{13}C NMR (D_2O , 50 MHz, δ , p.p.m.): 170.2, 150.2, 148.3, 148.1, 147.8, 147.4, 130.6, 130.3; DCI-MS (DCI is desorption chemical ionization) (*m/z*): 323 (MH^+ , 4), 322 (M^+ , 2). Compound (II) was obtained by dissolving (Ia) in a 1 M HCl aqueous solution, which on slow evaporation gave colourless rod-like crystals. Compound (IIIa) was obtained by dissolving (Ia) in a 1 M HClO_4 aqueous solution, which on slow evaporation yielded pale-yellow block-like crystals. Compound (IIIb) was obtained by dissolving (Ia) in an aqueous solution of $\text{Ag}[\text{PF}_6]$. On slow evaporation, pale-yellow block-like crystals were obtained.

Compound (Ia)

Crystal data

$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4$
 $M_r = 322.28$
 Monoclinic, $P2_1/c$
 $a = 10.4770$ (10) Å
 $b = 13.523$ (2) Å
 $c = 10.0580$ (10) Å
 $\beta = 110.070$ (10)°
 $V = 1338.5$ (3) Å³
 $Z = 4$

$D_x = 1.599$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 14\text{--}19^\circ$
 $\mu = 0.12$ mm⁻¹
 $T = 293$ (2) K
 Plate, pale yellow
 $0.46 \times 0.30 \times 0.11$ mm

Data collection

Stoe four-circle diffractometer
 $2\theta/\omega$ scans
 2356 measured reflections
 2336 independent reflections
 1227 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 12$
 $k = -16 \rightarrow 0$
 $l = -11 \rightarrow 11$
 3 standard reflections
 frequency: 60 min
 intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.092$
 $S = 0.90$
 2336 reflections
 258 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.014 (2)

Table 1

Hydrogen-bonding geometry (Å, °) for (Ia).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2O...O4 ⁱ	1.20 (4)	1.29 (4)	2.475 (3)	169 (3)
N3—H3N...N4	1.22 (3)	1.32 (3)	2.528 (3)	167 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_4 \cdot \text{Cl}^- \cdot 2.25\text{H}_2\text{O}$
 $M_r = 399.27$
 Monoclinic, $I2/a$
 $a = 19.5883$ (17) Å
 $b = 8.0623$ (5) Å
 $c = 22.936$ (2) Å
 $\beta = 90.559$ (11)°
 $V = 3622.0$ (5) Å³
 $Z = 8$

$D_x = 1.464$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5000 reflections
 $\theta = 2.1\text{--}25.9^\circ$
 $\mu = 0.26$ mm⁻¹
 $T = 293$ (2) K
 Rod, colourless
 $0.5 \times 0.2 \times 0.1$ mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
 13 718 measured reflections
 3488 independent reflections
 1943 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 25.9^\circ$
 $h = -24 \rightarrow 23$
 $k = -9 \rightarrow 9$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.093$
 $S = 0.82$
 3488 reflections
 327 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.027$
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 2

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2O...CH ⁱ	0.97 (4)	2.05 (4)	2.9996 (18)	168 (3)
N3—H3N...O4 ⁱⁱ	0.94 (3)	1.65 (3)	2.582 (3)	167 (2)
N4—H4N...O1W ⁱⁱⁱ	0.91 (3)	1.78 (3)	2.674 (3)	169 (3)
O1W—H1A...CH ^{iv}	0.83 (4)	2.30 (4)	3.112 (3)	167 (3)
O1W—H1B...O3 ^v	0.95 (4)	1.86 (4)	2.802 (3)	170 (3)
O2W—H21...Cl1	0.89 (9)	2.38 (10)	3.230 (6)	160 (6)
O2W—H22...O3 ^v	0.81 (9)	2.04 (10)	2.794 (6)	155 (8)
O3W—H31...O3 ^v	1.00 (10)	1.82 (10)	2.809 (9)	168 (7)
O3W—H32...Cl1	1.05 (14)	2.04 (14)	3.028 (9)	157 (9)
O4W—H41...Cl1 ^{vi}	0.84	2.50	3.344 (3)	179

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

Compound (IIIa)

Crystal data

$\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_4 \cdot \text{ClO}_4^- \cdot 3\text{H}_2\text{O}$
 $M_r = 476.79$
 Monoclinic, $P2_1/c$
 $a = 6.1401$ (7) Å
 $b = 15.6358$ (12) Å
 $c = 10.7154$ (8) Å
 $\beta = 106.934$ (8)°
 $V = 984.13$ (15) Å³
 $Z = 2$

$D_x = 1.609$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5000 reflections
 $\theta = 1.7\text{--}26.1^\circ$
 $\mu = 0.27$ mm⁻¹
 $T = 223$ (2) K
 Block, pale yellow
 $0.36 \times 0.35 \times 0.26$ mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
 7650 measured reflections
 1914 independent reflections
 1419 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 25.9^\circ$
 $h = -7 \rightarrow 7$
 $k = -19 \rightarrow 19$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\max} < 0.001$
1914 reflections	$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
190 parameters	$\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$

Table 3
Hydrogen-bonding geometry (\AA , $^\circ$) for (IIIa).

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2O...O2 ⁱ	1.20	1.20	2.392 (3)	177 (4)
N2—H2N...O1W	0.91 (2)	1.78 (3)	2.684 (2)	172 (2)
O1W—H1A...O1 ⁱⁱ	0.84 (3)	1.94 (3)	2.734 (2)	156 (3)
O1W—H1B...O1	0.86 (3)	1.98 (3)	2.830 (2)	172 (3)
O2W—H2WA...O2 ⁱⁱⁱ	1.06	1.85	2.889 (2)	167

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

Compound (IIIb)

Crystal data

$\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_4 \cdot \text{PF}_6^- \cdot 3\text{H}_2\text{O}$	$D_x = 1.722 \text{ Mg m}^{-3}$
$M_r = 522.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5000 reflections
$a = 6.1910 (6) \text{ \AA}$	$\theta = 1.7\text{--}26.1^\circ$
$b = 15.6564 (11) \text{ \AA}$	$\mu = 0.24 \text{ mm}^{-1}$
$c = 10.8349 (10) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 106.400 (11)^\circ$	Rod, pale yellow
$V = 1007.48 (15) \text{ \AA}^3$	$0.70 \times 0.20 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Stoe IPDS diffractometer	$R_{\text{int}} = 0.029$
φ oscillation scans	$\theta_{\text{max}} = 25.9^\circ$
7713 measured reflections	$h = -7 \rightarrow 7$
1944 independent reflections	$k = -19 \rightarrow 19$
1628 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1018P)^2 + 0.1313P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.152$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.20$	$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
1944 reflections	$\Delta\rho_{\min} = -0.83 \text{ e } \text{\AA}^{-3}$
186 parameters	
All H-atom parameters refined	

Table 4
Hydrogen-bonding geometry (\AA , $^\circ$) for (IIIb).

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2O...O2 ⁱ	1.21	1.21	2.405 (4)	171 (6)
N2—H2N...O1W	0.91 (3)	1.77 (3)	2.683 (3)	177 (3)
O1W—H1WA...O1 ⁱⁱ	0.79 (4)	1.98 (4)	2.739 (2)	160 (4)
O1W—H1WB...O1	0.89 (4)	1.96 (4)	2.841 (3)	171 (4)
O2W—H2WA...O2 ⁱⁱⁱ	0.89	2.07	2.815 (4)	140

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

The H atoms were located from difference Fourier maps and refined isotropically, including the pyNH and CO₂H H atoms. For compounds (Ia) and (II), the hydrogen bonds involving these H atoms are of the unusual symmetric type, hence the long N—H, H...N, O—H and O...H distances. This type of hydrogen bond, N—H...N for example, with identical bond distances and angles, has been observed previously and analysed theoretically by Bock *et al.* (1992). In compound (II), water molecules O2W and O3W are the same atom but disordered over two sites, with refined occupancies of 0.62 and 0.38. In compound (IIIa), the perchlorate anion possesses C₂ symmetry and atoms O12, O13 and O14 are disordered. In some cases, the water H atoms could be located from difference Fourier maps and were refined isotropically. When the refinement was unstable in the final cycles of refinement they were held fixed, as were water O4W in (II) and O2W in (IIIa) and (IIIb) ($U_{\text{iso}} = 0.1 \text{ \AA}^2$).

For compound (Ia), data collection: STADIA (Stoe & Cie, 1997); cell refinement: STADIA; data reduction: X-RED in STADIA. For compounds (II), (IIIa) and (IIIb), data collection: EXPOSE (Stoe & Cie, 2000); cell refinement: CELL (Stoe & Cie, 2000). For (II) and (IIIb), data reduction: INTEGRATE (Stoe & Cie, 2000). For (IIIa), data reduction: X-RED in STADIA. For all four compounds, program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON99 (Spek, 1990); software used to prepare material for publication: SHELXL97.

Financial support from the Swiss National Science Foundation is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1159). Services for accessing these data are described at the back of the journal.

References

- Alfonso, M., Wang, Y. & Stoeckli-Evans, H. (2001). *J. Chem. Soc. Dalton Trans.* In the press.
- Bock, H., Vauple, T., Näther, C., Ruppert, K. & Havlas, Z. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 299–301.
- Goodwin, H. A. & Lions, F. (1959). *J. Am. Chem. Soc.* **81**, 6415–6421.
- Karanović, L., Poleti, D., Bogdanović, G. A. & Spasojević-De Biré, A. (1999). *Acta Cryst.* **C55**, 911–913.
- Krol, I. A., Agre, V. M., Trunov, V. K. & Avdonina, L. M. (1983). *Koord. Khim.* **9**, 687–693.
- Lynch, D. E., Smith, G., Byriel, K. A., Kennard, C. H. L. & Whitaker, A. K. (1994). *Aust. J. Chem.* **47**, 309–313.
- Robertson, K. N., Bakshi, P. K., Lantos, S. D., Cameron, T. S. & Knop, O. (1998). *Can. J. Chem.* **76**, 583–611.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Stoe & Cie (1997). *STADIA*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (2000). *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS Software*. Version 2.93. Stoe & Cie, Darmstadt, Germany.