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Self-assembled hydrogen-bonded bilayers in 1,4-diazabicyclo[2.2.2]-octane–*N*-(phosphonomethyl)imino-diacetic acid–water (1/1/1.5)

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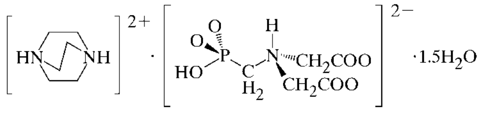
The title compound is a hydrated salt, 1,4-diazoniabicyclo[2.2.2]octane–*N*-[(hydroxyphosphinato)methyl]iminiodiacetate–water (1/1/1.5), $C_6H_{14}N_2^{2+}\cdot C_5H_8NO_7P^{2-}\cdot 1.5H_2O$, in which one of the water molecules lies across a twofold rotation axis in space group $P2/n$. The ionic components are linked into sheets by a combination of a three-centre N—H···(O)$_2$ hydrogen bond and two-centre O—H···O and N—H···O hydrogen bonds, and these sheets are pairwise linked by the water molecules into bilayers, by means of further O—H···O hydrogen bonds.

Comment

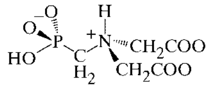
Phenylphosphonic acid, PhP(O)(OH)$_2$, generates a wide diversity of supramolecular structures in combination with amines (Ferguson *et al.*, 1998), and exploratory studies of the related diacids ethane-1,2-diphosphonic acid (Glidewell *et al.*, 2000; Wheatley *et al.*, 2001) and phosphonoacetic acid (Farrell *et al.*, 2001) indicate that these are both potentially versatile building blocks for supramolecular chemistry. Accordingly, we have now initiated a study of the related triacid *N*-(phosphonomethyl)iminodiacetic acid, (HO)$_2$P(O)CH$_2$N(CH$_2$COOH)$_2$, and report here the structure of the hydrated adduct, (I), formed with 1,4-diazabicyclo[2.2.2]octane (DABCO).

When cocrystallized from methanol exposed to air, *N*-(phosphonomethyl)iminodiacetic acid and DABCO generate the sesquihydrate salt $C_6H_{14}N_2^{2+}\cdot C_5H_8NO_7P^{2-}\cdot 1.5H_2O$, (I) (Fig. 1), in which two H atoms have been transferred to the diamine to generate the [HN(CH$_2$CH$_2$)$_3$NH]$^{2+}$ cation, while in the anion, the N atom is protonated, leaving only one H atom bonded to O, resulting in the [HOP(O)$_2$CH$_2$N(H)(CH$_2$COO)$_2$]$^{2-}$ anion. One water molecule, containing atom O9, lies across a twofold rotation axis, selected as that along $(\frac{1}{4},y,\frac{3}{4})$, while the water molecule containing atom O8 lies in a general position.

There are three N—H···O contacts within the anion of (I), all between the positively charged N—H unit and the negatively charged atoms O2, O4 and O6. Although the N—H···O angles are all small (Table 2), these contacts may nonetheless be significant in controlling the overall conformation of the anion. In addition to these interactions, there are seven genuine hydrogen bonds, four of the two-centre O—H···O type, one of the two-centre N—H···O type and an asymmetric three-centre N—H···(O)$_2$ system (Table 2). Together, these link the independent components into a two-dimensional structure, which is readily analysed using the substructure approach (Gregson *et al.*, 2000). The anions alone form simple chains, while the anions and cations together form single sheets, and these are linked in pairs by the water molecules to form bilayers.



(I)



(II)

The phosphonic atom O5 in the anion at (x, y, z) acts as a hydrogen-bond donor to carboxylate atom O4 in the anion at (x, $y - 1$, z), so generating by translation a $C(8)$ chain parallel to the [010] direction (Fig. 2). Four of these chains run through each unit cell, and chains related to one another by the action of the n glide plane are linked into sheets by the cations. In the cation at (x, y, z), atom N11 is linked by the two-centre N—H···O hydrogen bond to atom O6 in the anion at (x, y, z), while atom N21 forms a planar three-centre system with atoms O1 and O2 in the anion at ($\frac{1}{2} + x$, $2 - y$, $z - \frac{1}{2}$), so forming a $C_2^2(13)$ chain along $[10\overline{1}]$ generated by the n glide plane at $y = 1$ (Fig. 2). The combination of [010] and $[10\overline{1}]$ chains produces a (101) sheet, in which the rings defined by the shorter component of the three-centre hydrogen bond are of the $R_6^6(38)$ type (Fig. 2).

Pairs of (101) sheets related by the twofold rotation axis are linked into bilayers by the water molecules, whose action is most readily analysed in terms of the substructure they form with the anions. Water atom O8 at (x, y, z) acts as a hydrogen-bond donor, *via* atoms H81 and H82, respectively, to carboxylate atom O1 in the anion at (x, y, z) and to phosphonate atom O7 in the anion at ($x - \frac{1}{2}$, $1 - y$, $\frac{1}{2} + z$). Propagation of these two hydrogen bonds produces a $C_2^2(10)$ chain along $[10\overline{1}]$ generated by the n glide plane at $y = \frac{1}{2}$ (Fig. 3). Water atom O9 at $(\frac{1}{4},y,\frac{3}{4})$ acts as a hydrogen-bond donor to water O8 atoms at (x, y, z) and at ($\frac{1}{2} - x$, y, $\frac{3}{2} - z$), which lie in adjacent $C_2^2(10)$ chains. Hence, the anions and the water molecules together form a molecular ladder along $[10\overline{1}]$, with the $C_2^2(10)$ chains playing the role of the uprights and the

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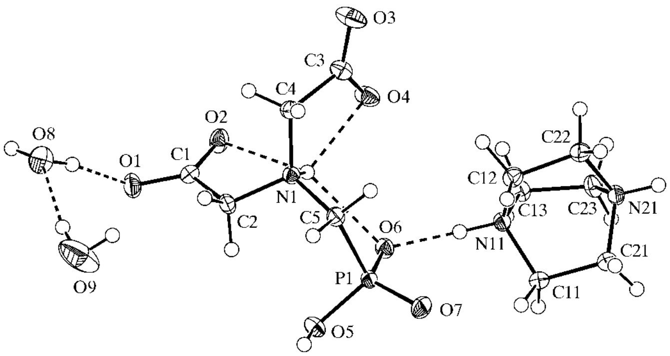

Figure 1
The molecular components of compound (I), showing the atom-labelling scheme. Atom O9 lies on a twofold rotation axis. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

O9 water molecule forming the rungs. Alternatively, this substructure can be regarded as a chain of edge-fused $R_8^8(28)$ rings (Fig. 3). The overall effect of the water molecules is the linking of the cation–anion sheets (Fig. 2) into a (101) bilayer, and it is clear that these water molecules are an integral and essential component of the supramolecular structure of (I).

All of the H atoms were clearly revealed in difference maps, and their locations are consistent with the observed P—O and C—O distances in the anion and the N—C distances in the cation (Table 1). As noted earlier, the pseudo-trigonal conformation of the anion may be influenced by the intramolecular N—H···O contacts. The N—C—C—N torsion angles (Table 1) in the cation indicate a very substantial deviation from the idealized D_{3h} ($\bar{6}m2$) molecular symmetry, induced, as usual, by the avoidance of perfect eclipsing in the –CH$_2$—CH$_2$– units.

In view of the two-dimensional supramolecular structure of (I), it is of interest to compare this with the structure of the acid component itself, (II) [Cambridge Structural Database (CSD; Allen & Kennard, 1993) reference code BOWJIG (Shkol'nikova *et al.*, 1982)], which crystallizes in space group $P\bar{1}$. The CSD entry for BOWJIG lists coordinates for only nine of the ten H atoms and notes that the coordinates for the H atom on one of the carboxyl atoms, O4, have been omitted

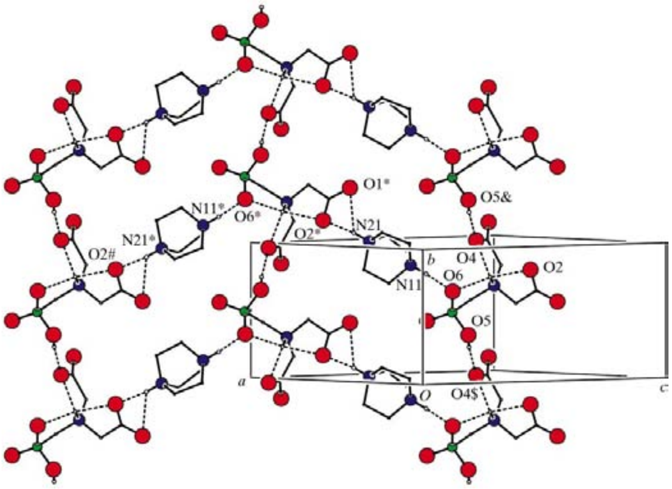

Figure 2
Part of the crystal structure of (I), showing the formation of a (101) sheet built from cations and anions only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(\frac{1}{2}+x, 2-y, z-\frac{1}{2})$, $(1+x, y, z-1)$, $(x, y-1, z)$ and $(x, 1+y, z)$, respectively.

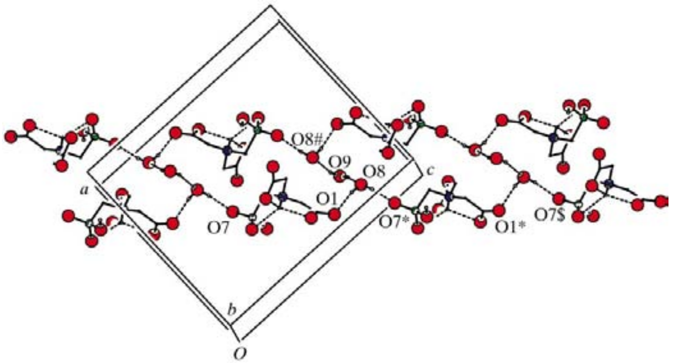

Figure 3
Part of the crystal structure of (I), showing the formation of a molecular ladder along $[10\bar{1}]$ built from anions and water molecules only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(x-\frac{1}{2}, 2-y, \frac{1}{2}+z)$, $(\frac{1}{2}-x, y, \frac{3}{2}-z)$ and $(x-1, y, 1+z)$, respectively.

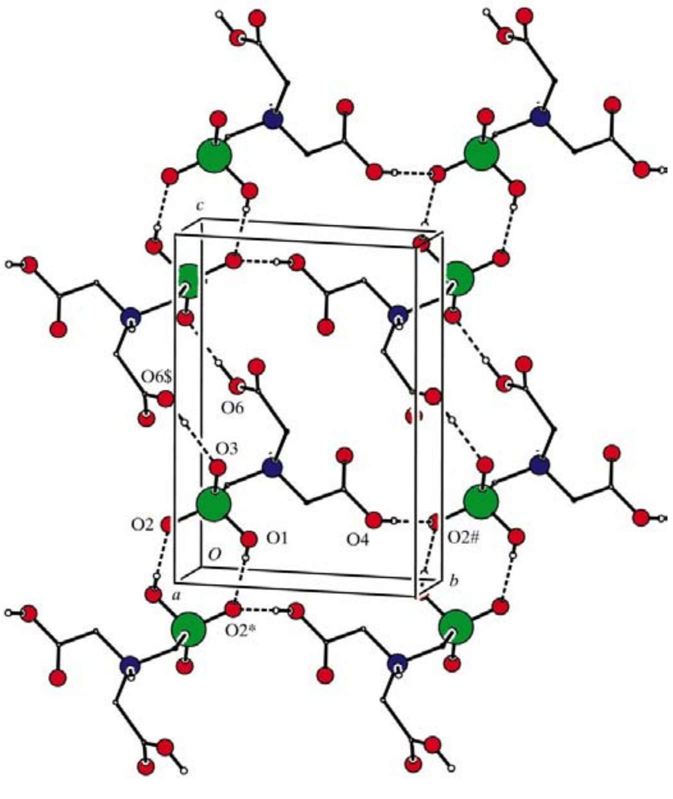

Figure 4
Part of the crystal structure of BOWJIG (Shkol'nikova *et al.*, 1982), showing the formation of a (110) sheet built from four types of centrosymmetric ring. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(-x, -y, -z)$, $(x-1, 1+y, z)$ and $(-x, -y, 1-z)$, respectively.

from the entry because of suspected error. The coordinates for this missing H atom have been estimated by assuming that it lies on the line O4···O2^{iv} [symmetry code: (iv) $x - 1, 1 + y, z$], where the O···O distance is 2.598 Å, with an assumed bonded O—H distance of 0.84 Å. Subject to these assumptions, compound (II), which has the zwitterionic constitution $(HOCOCH_2)_2N(H)CH_2P(O)_2OH$, forms a hydrogen-bonded supramolecular structure which is three-dimensional. The intermolecular O—H···O hydrogen bonds link the molecules into very elegant (110) sheets built from four types of ring, all centrosymmetric, of the $R_2^2(8)$, $R_2^2(16)$, $R_4^2(20)$ and $R_4^4(24)$ types (Fig. 4), while a single N—H···O hydrogen bond links each such sheet to its two neighbours, so generating a single three-dimensional framework. It is notable that (II) contains an $R_2^2(8)$ motif generated by the phosphonic acid units, while the very common $R_2^2(8)$ motif so characteristic of carboxylic acids is absent.

Experimental

To prepare salt (I), equimolar quantities of the two organic components *N*-(phosphonomethyl)iminodiacetic acid and 1,4-diazabicyclo[2.2.2]octane were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, exposed to the laboratory atmosphere, providing analytically pure (I). Analysis, found: C 36.1, H 7.3, N 11.5%; $C_{22}H_{50}N_6O_{17}P_2$ requires: C 36.1, H 6.9, N 11.5%. Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{14}N_2^{2+}\cdot C_5H_8NO_7P^{2-}\cdot 1.5H_2O$
$M_r = 366.31$
Monoclinic, $P2/n$
$a = 14.1042$ (5) Å
$b = 7.0560$ (3) Å
$c = 16.4004$ (7) Å
$\beta = 90.1130$ (18)°
$V = 1632.15$ (11) Å^3
$Z = 4$

$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3693 reflections
$\theta = 2.9$–27.5°
$\mu = 0.22$ mm^{-1}
$T = 150$ (2) K
Needle, colourless
0.16 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
12 611 measured reflections
3693 independent reflections
2841 reflections with $I > 2\sigma(I)$

$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 8$
$l = -21 \rightarrow 21$

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.499 (2)	P1—O5	1.5685 (12)
N1—C4	1.499 (2)	P1—O6	1.5083 (12)
N1—C5	1.508 (2)	P1—O7	1.4934 (12)
N11—C11	1.494 (2)	P1—C5	1.8253 (17)
N11—C12	1.497 (2)	C1—O1	1.247 (2)
N11—C13	1.493 (2)	C1—O2	1.262 (2)
N21—C21	1.493 (2)	C3—O3	1.231 (2)
N21—C22	1.499 (2)	C3—O4	1.275 (2)
N21—C23	1.498 (2)		
O1—C1—C2—N1	−166.7 (2)	N11—C11—C21—N21	−17.5 (2)
O3—C3—C4—N1	−171.7 (2)	N11—C12—C22—N21	−16.9 (2)
O7—P1—C5—N1	168.3 (2)	N11—C13—C23—N21	−17.2 (2)

Table 2
Hydrogen bonds and short intramolecular contacts (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.93	2.33	2.682 (2)	102
N1—H1···O4	0.93	2.08	2.591 (2)	113
N1—H1···O6	0.93	2.42	2.973 (2)	118
O5—H5···O4^{i}	0.84	1.69	2.507 (2)	162
N11—H11···O6	0.93	1.68	2.590 (2)	165
N21—H21···O1^{ii}	0.93	2.43	3.062 (2)	125
N21—H21···O2^{ii}	0.93	1.75	2.673 (2)	173
O8—H81···O1	0.84	1.99	2.815 (2)	166
O8—H82···O7^{iii}	0.84	1.94	2.770 (2)	171
O9—H9···O8	0.84	2.07	2.891 (2)	167

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 1.03$
3693 reflections
216 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.6209P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0059 (14)

Compound (I) crystallized in the monoclinic system; space group *P*2/*n* or *Pn* was assumed from the systematic absences and *P*2/*n* was established by the analysis. H atoms were treated as riding atoms, with C—H = 0.99, N—H = 0.93 and O—H = 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1565). Services for accessing these data are described at the back of the journal.

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