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Conformational isomers of the [(5-methyl-2-pyridinio)aminomethylene]diphosphonate dianion and [(5-methyl-2-pyridyl)aminomethylene]diphosphonate trianion in salts with 4-aminopyridine and ammonia

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The crystal structures of two salts, products of the reactions between [(5-methyl-2-pyridyl)aminomethylene]bis(phosphonic acid) and 4-aminopyridine or ammonia, namely bis(4-aminopyridinium) hydrogen [(5-methyl-2-pyridinio)aminomethylene]diphosphonate 2.4-hydrate, $2C_5H_7N_2^{+}\cdot C_7H_{10}N_2O_6P_2^{2-}\cdot 2.4H_2O$, (I), and triammonium hydrogen [(5-methyl-2-pyridyl)aminomethylene]diphosphonate monohydrate, $3NH_4^{+}\cdot C_7H_9N_2O_6P_2^{3-}\cdot H_2O$, (II), have been determined. In (I), the *Z* configuration of the ring N—C and amino N—H bonds of the bisphosphonate dianion with respect to the $C_{ring}—N_{amino}$ bond is consistent with that of the parent zwitterion. Removing the H atom from the pyridyl N atom results in the opposite *E* configuration of the bisphosphonate trianion in (II). Compound (I) exhibits a three-dimensional hydrogen-bonded network, in which 4-aminopyridinium cations and water molecules are joined to ribbons composed of anionic dimers linked by O—H···O and N—H···O hydrogen bonds. The supramolecular motif resulting from a combination of these three interactions is a common phenomenon in crystals of all of the *Z*-isomeric zwitterions of 4- and 5-substituted (2-pyridylaminomethylene)bis(phosphonic acid)s studied to date. In (II), ammonium cations and water molecules are linked to chains of trianions, resulting in the formation of double layers.

Comment

The (2-pyridylaminomethylene)bis(phosphonic acid)s, a subclass of bisphosphonates with a direct $C\alpha—N_{amino}$ bond, demonstrate a broad spectrum of activities. There is a vast literature dealing with their herbicidal properties (Suzuki *et al.*, 1979; Cromartie *et al.*, 1999; Kafarski *et al.*, 2000; Forlani *et al.*, 2007). Recently, they have also been shown to be promising antimalarial, anti-amoebic (Ghosh *et al.*, 2004) and antibacterial (Leon *et al.*, 2006) agents, as well as stimulators of human $\gamma\delta$T cells of the immune system (Sanders *et al.*, 2004). All these activities correlate well with their inhibitory potency with respect to the FPP synthase, a key regulatory enzyme of the mevalonate pathway found to be a major target of nitrogen-containing bisphosphonates in human, parasite and plant cells (Cromartie *et al.*, 1999; Sanders *et al.*, 2003; Coxon *et al.*, 2006). Interestingly, the topology, size and/or chemical nature of the substituent on the pyridyl ring clearly play a role in the biological activity of this class of acids.

Spectroscopic and X-ray studies of (2-pyridylaminomethylene)bis(phosphonic acid)s to date have revealed a clear relationship between the topology of the substituents on the ring and their conformational preferences. A slight predominance of the *Z* over the *E* geometrical isomer (defined here as the C1—N1—C2—C3 torsion angle being close to 0 or 180°, respectively; see Fig. 1 for atom numbering) has been observed in solutions of compounds substituted at the 4- or 5-position, and as a result the dominant isomer has been observed to crystallize [Cambridge Structural Database (CSD; Allen, 2002) refcodes JEDYAT (Matczak-Jon *et al.*, 2006*a*), QURYEH (Matczak-Jon *et al.*, 2001), BEKCAW and BEKBUP (Sanders *et al.*, 2003), and YEFWIQ (Matczak-Jon *et al.*, 2006*b*)]. On the other hand, the 3-pyridyl-substituted compounds demonstrate the opposite *E* configuration in the solid state [QURYAD (Matczak-Jon *et al.*, 2001) and MUQDIL (Szabo *et al.*, 2002)], and the same isomer is

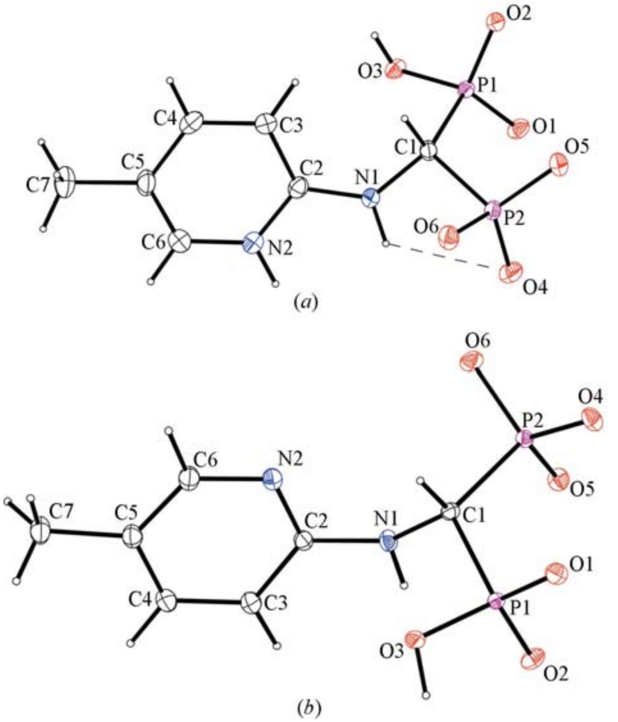

Figure 1
The molecular structures of (*a*) the dianion in (I) and (*b*) the trianion in (II), showing the atom-numbering schemes and the intramolecular N—H···O hydrogen bond in (I) (dashed line). Displacement ellipsoids are drawn at the 50% probability level.

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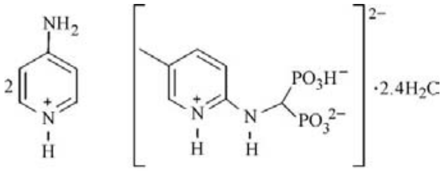
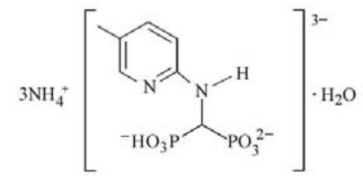
expected to dominate in their solutions (Matczak-Jon, 2005). Interestingly, (2-pyridylaminomethylene)bis(phosphonic acid), with equal populations of *Z* and *E* in solution, crystallizes as the *E* isomer (JEDXUM; Matczak-Jon *et al.*, 2006*a*). In all these crystals, except for the disodium salt of the 5-chloro derivative (BEKBUP; Sanders *et al.*, 2003), the bisphosphonic acid components exist as zwitterions with a proton transfer from one of the phosphonic acid groups to pyridyl atom N2.

We report here the crystal structures of two [(5-methyl-2-pyridyl)aminomethylene]diphosphonate salts with different ionization states of the anion, namely [(5-methyl-2-pyridinio)aminomethylene]diphosphonate in (I) and [(5-methyl-2-pyridyl)aminomethylene]diphosphonate in (II).



(I)



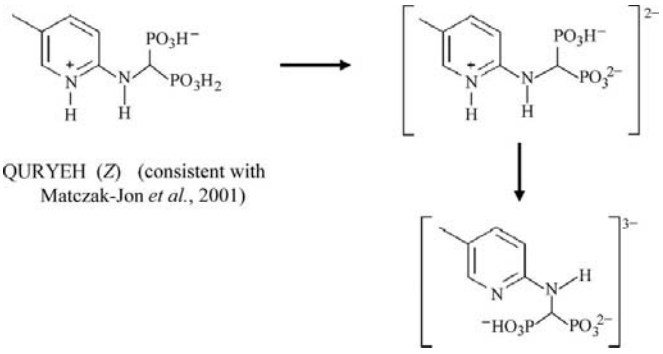
(II)

Our results are of interest for a number of reasons. Firstly, only a few crystal structures have been determined to date of salts containing bisphosphonate anions with a direct Cα—N$_{\rm amino}$ bond (Mao *et al.*, 2006; Sanders *et al.*, 2003; Bon *et al.*, 2008). In particular, the only example reported for a (2-pyridylaminomethylene)bis(phosphonic acid) is the disodium salt of [(5-chloro-2-pyridyl)aminomethylene]diphosphonate. In addition, we provide for the first time the X-ray crystal structure of the organic salt formed between a member of this particular class of acids and an amine. Secondly, we demonstrate a correlation between the protonation state of the [(5-methyl-2-pyridyl)aminomethylene]diphosphonate anion and its conformational preferences. Finally, we provide evidence that the deprotonation of the parent bisphosphonate (Matczak-Jon *et al.*, 2001) proceeds in the manner shown in the scheme below. This is surprisingly in contrast to the related 5-Cl derivative, where the crystal structure of its disodium salt (Sanders *et al.*, 2003) reveals both phosphonate groups monoprotonated and a neutral pyridyl atom.

The asymmetric unit of (I) consists of one bisphosphonate dianion, two 4-aminopyridinium cations and 2.4 water molecules (with O1*W* and disordered O2*W* in general positions, and partially occupied O3*W* on a twofold axis). In the 4-aminopyridinium cations, the amine groups (N41 and N42) are neutral and positive charges are located at pyridinium atoms N11 and N12. The asymmetric unit of (II) contains one trianion, three ammonium cations (N10, N20 and N30) and one water molecule (O1*W*). It should be noted that, depending on the protonation state [the pyridyl atom N2 is protonated in (I) but not in (II)], the bisphosphonate anion adopts opposite *Z* or *E* configurations, as defined above, with respect to the C2—N1 bond. This is reflected in the C1—N1—C2—C3 torsion angle of 10.3 (2)° in (I) and −147.18 (9)° in (II) (Fig. 1).

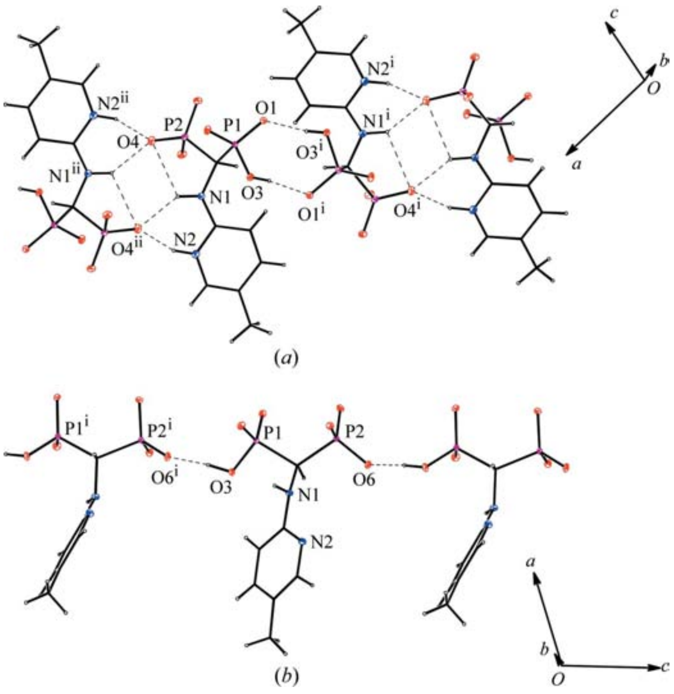
It is a general rule in the structures known so far that, because of the formal sp^2-hybridization of atom N1 and the partial double-bond character of the C2—N1 linkage, both atoms N1 and C1 are coplanar with the pyridyl ring. Similarly, this is observed in (I) and (II) (Fig. 1, and Tables 1 and 3). However, as seen from the C1—N1—C2—N2 and C1—N1—C2—C3 torsion angles, atom C1 is displaced more from the pyridyl ring plane in (II) than in (I) [at 0.65 (1) and 0.39 (1) Å, respectively]. Moreover, in (II), some degree of pyramidalization of atom N1 is evident. The sum of the angles at N1 is 347.3 (1)°, which indicates that hybridization of the N1 atom is not purely sp^2. As a result, the C2—N1 bond in (II) is slightly longer [1.385 (2) Å compared with 1.346 (2) Å in (I)].

The geometry of the diphosphonate fragment in (II) is in good agreement with that of parent zwitterion (QURYEH; Matczak-Jon *et al.*, 2001; see scheme below). The O3—P1—C1—P2—O6 sequence, with one protonated and one deprotonated O atom, reveals a typical, almost planar *W* conformation. Thus, every P atom is antiperiplanar to one of the O atoms from the adjacent phosphonate group and synclinal to the remaining O atoms from that group. However, in (I) the *W* conformation is slightly distorted (see the relevant torsion angles in Table 1). This seems to be of some importance for the formation of intermolecular interactions. The orientation of the phosphonate groups in relation to the pyridyl ring is defined by the C2—N1—C1—P1 and C2—N1—C1—P2 torsion angles, which reveal that in both (I) and (II), atoms P1 and P2 have an anticlinal orientation with respect to pyridyl atom C2. However, a comparison of these values with those reported previously indicates that the $^{-}HO_3P—C—PO_3^{2-}$ diphosphonate portion is slightly more perpendicular with respect to the pyridyl ring than in the parent zwitterion and related 4-methyl, 5-chloro and 5-bromo derivatives. The planes defined by the pyridyl ring and the P1—C1—P2 linkage intersect with each other at 68.7 (1)° in (I) and 66.2 (1)° in (II).



Consistent with previous observations, in both (I) and (II) the geometries of both the monoprotonated (PO_3H^-) and the completely deprotonated (PO_3^{2-}) groups deviate significantly from ideal tetrahedra. This is mainly reflected in the high values of the O1—P1—O2 and O4—P2—O5 angles, in which the unprotonated O atoms are involved. On the other hand, the (H)O3—P1—C1 angle, in which the protonated O atom is involved, has the smallest value in both (I) and (II) (Tables 1 and 3).

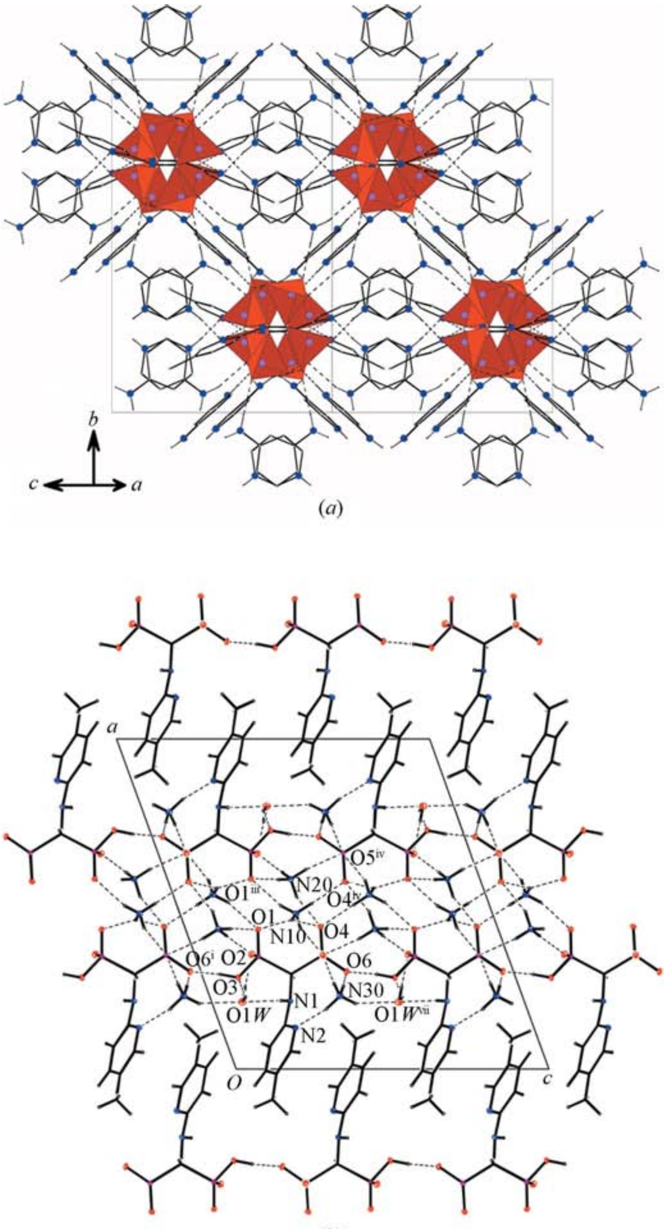
The common structural motifs in the crystal structures of (2-pyridylaminomethylene)bis(phosphonic acid) and its 4- and 5-substituted derivatives reported to date (Matczak-Jon *et al.*, 2001, 2006*a*,*b*; Sanders *et al.*, 2003) are chains and molecular dimers formed by the adjacent zwitterions. Usually these two types of motifs give rise to ribbons, in which some N—H···O and C—H···O contacts play a role. In (I), the strongest interactions (O3—H3···O1^{i}; symmetry code as in Table 2) join the twofold-axis-related dianions to form dimers *via* an $R_2^2(8)$ ring motif. Each dimer is linked with two adjacent dimers by centrosymmetric bifurcated N1—H2···O4^{ii} and N2—H4···O4^{ii} hydrogen bonds to the same O4 atom, which is also involved in the weak intramolecular N1—H2···O4 contact and therefore becomes a trifurcated acceptor. The combination of three N—H···O4 contacts gives rise to $R_2^1(6)$ and $R_2^2(4)$ rings (Fig. 2*a* and Table 2). As a result, ribbons running in the [101] direction are formed, as shown in Fig. 3(*a*). It is also worth noting that the structural motif comprising the intermolecular O—H···O and N1—H···O contacts, as presented in Fig. 2(*a*), is a common feature in all *Z*-isomeric zwitterions studied to date. On the other hand, the deformed *W* conformation of the O3—P1—C1—P2—O6 sequence disfavours chain formation in (I). A quite different structural motif is observed in (II), where the removal of the H atom on atom N2 relaxes a strain imposed on the *Z* configuration by the N2—H4···O hydrogen bond, which allows a conformational switch of trianions *via* rotation around the C2—N1 bond. As a result, the optimal conformation of the [(5-methyl-2-pyridyl)-aminomethylene]diphosphonate trianion in (II) is a pseudo-*E* isomer, with an almost planar O3—P1—C1—P2—O6 sequence. This enables atoms O3 and O6 from adjacent glide-plane-related anions to interact with each other *via* strong O3—H3···O6^{i} hydrogen bonds to form infinite chains along the *c* axis (Fig. 2*b* and Table 4).



(*a*)

(*b*)

Figure 2
The arrangement of (*a*) the dianions in (I) within the ribbons running in the [101] direction, and (*b*) the trianions in (II) within the infinite chains along the *c* axis. Dashed lines indicate O—H···O and N—H···O hydrogen bonds. Symmetry codes are given in Tables 2 and 4.



(*a*)

(*b*)

Figure 3
The crystal packing modes in the structures of (I) and (II), showing (*a*) the anionic ribbons joined by the 4-aminopyridinium cations to form a three-dimensional structure, and (*b*) the double layers made up from anionic chains in a head-to-head arrangement with NH_4^+ cations and water molecules located between them. O—H···O and N—H···O hydrogen bonds are shown with dashed lines. Water molecules in (I) have been omitted for clarity; the shaded tetrahedra represent the phosphonate groups. Symmetry codes for (II) are given in Table 4.

The crystal packing of (I) and (II) is greatly affected by the presence of the 4-aminopyridinium and ammonium cations, respectively. In (I), both the amine (N41 and N42) and the pyridinium (N11 and N12) N atoms along with the water O atoms form N—H⋯O and O—H⋯O hydrogen bonds with the phosphonate O atoms from the ribbons (Fig. 3*a* and Table 2). Moreover, phosphonate atoms O2 and O6 are involved in bifurcated N—H⋯O contacts. All that, together with the extensive network of C—H⋯O/N contacts and the weak C6—H16⋯Cg^{ii} interaction [symmetry code as in Table 2; H⋯Cg^{ii} = 2.61 (2) Å, C⋯Cg^{ii} = 3.531 (2) Å and C—H⋯Cg^{ii} = 164 (2)°, where *Cg* is the centroid of the phenyl ring of the cation defined by atoms N11/C21–C61], and the stacking between the 4-aminopyridinium cations [$Cg\cdots Cg^{iv}$ = 3.460 (1) Å], gives rise to a three-dimensional network in the crystal structure. In (II), adjacent chains are arranged in a head-to-head manner, with the ammonium cations and water molecules located between the methylenediphosphonate groups. Numerous H_3N—H⋯O interactions and one H_3N—H⋯N contact link the ammonium cations with the hydrophilic parts of the dianions (and water molecules), giving rise to the double layers parallel to the (100) plane (Fig. 3*b*). Such crystal architecture leads to the aggregation of the hydrophilic and hydrophobic groups into two distinct regions in the crystal structure.

Experimental

To obtain (I), [(5-methyl-2-pyridyl)aminomethylene]bis(phosphonic acid) (0.0565 g, 0.2 mmol) and 4-aminopyridine (0.0376 g, 0.4 mmol) were dissolved in water (5 ml) and heated under reflux for *ca* 7 h. Crystals of (I) were obtained after slow concentration of the resulting solution combined with diffusion of 2-propanol. Crystals of (II) were prepared by slow evaporation of a 5 ml solution of [(5-methyl-2-pyridyl)aminomethylene]bis(phosphonic acid) (0.0565 g, 0.2 mmol) dissolved in 10% ammonia.

Compound (I)

Crystal data

$2C_5H_7N_2^+\cdot C_7H_{10}N_2O_6P_2^{2-}\cdot 2.4H_2O$
M_r = 513.60
Monoclinic, $C2/c$
a = 20.385 (3) Å
b = 17.838 (3) Å
c = 13.038 (3) Å
β = 101.89 (3)°
V = 4639.3 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 100 K
0.30 × 0.25 × 0.22 mm

Data collection

Kuma KM-4-CCD κ-geometry diffractometer with Sapphire CCD camera
38561 measured reflections
6761 independent reflections
5813 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.103
S = 1.07
6761 reflections
408 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Compound (II)

Crystal data

$3NH_4^+\cdot C_7H_9N_2O_6P_2^{3-}\cdot H_2O$
M_r = 351.24
Monoclinic, $P2_1/c$
a = 17.087 (3) Å
b = 6.216 (2) Å
c = 15.159 (3) Å
β = 109.84 (3)°
V = 1514.5 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 100 K
0.40 × 0.30 × 0.05 mm

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

P1—O1	1.5124 (9)	P2—O6	1.5339 (10)
P1—O2	1.4991 (10)	P2—C1	1.8425 (13)
P1—O3	1.5860 (10)	N1—C1	1.460 (2)
P1—C1	1.8403 (12)	N1—C2	1.346 (2)
P2—O4	1.5169 (10)	N2—C2	1.348 (2)
P2—O5	1.5199 (10)	N2—C6	1.353 (2)
O1—P1—O2	116.23 (6)	O4—P2—C1	105.84 (6)
O1—P1—O3	110.02 (6)	O5—P2—C1	108.13 (6)
O2—P1—O3	107.74 (5)	O6—P2—C1	104.42 (5)
O1—P1—C1	107.82 (5)	C1—N1—C2	125.05 (11)
O2—P1—C1	111.56 (5)	C1—N1—H2	117.5 (13)
O3—P1—C1	102.61 (5)	C2—N1—H2	116.6 (13)
O4—P2—O5	114.25 (6)	P1—C1—P2	117.93 (6)
O4—P2—O6	111.10 (6)	P1—C1—N1	112.16 (8)
O5—P2—O6	112.34 (5)	P2—C1—N1	106.53 (8)
O1—P1—C1—P2	−82.24 (8)	O3—P1—C1—N1	37.33 (9)
O2—P1—C1—P2	46.54 (9)	O4—P2—C1—N1	50.11 (9)
O3—P1—C1—P2	161.63 (6)	O5—P2—C1—N1	172.95 (7)
O4—P2—C1—P1	−76.95 (8)	O6—P2—C1—N1	−67.24 (9)
O5—P2—C1—P1	45.89 (8)	C2—N1—C1—P1	−102.04 (12)
O6—P2—C1—P1	165.71 (7)	C2—N1—C1—P2	127.53 (11)
O1—P1—C1—N1	153.46 (8)	C1—N1—C2—N2	−168.82 (11)
O2—P1—C1—N1	−77.77 (9)	C1—N1—C2—C3	10.3 (2)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O3—H3⋯$O1^{i}$	0.81 (3)	1.75 (3)	2.556 (2)	173 (3)
N1—H2⋯O4	0.95 (2)	2.50 (2)	2.934 (2)	108 (2)
N1—H2⋯$O4^{ii}$	0.95 (2)	2.02 (2)	2.841 (2)	143 (2)
N2—H4⋯$O4^{ii}$	0.93 (2)	1.71 (2)	2.599 (2)	159 (2)
N11—H11⋯O5	0.87 (2)	1.75 (2)	2.618 (2)	172 (2)
N41—H41*A*⋯$O2^{iii}$	0.87 (2)	2.02 (2)	2.885 (2)	174 (2)
N41—H41*B*⋯$O1^{iv}$	0.87 (2)	2.14 (2)	2.979 (2)	161 (2)
N12—H12⋯O6	0.93 (2)	1.73 (2)	2.658 (2)	174 (2)
N42—H42*A*⋯$O2^{v}$	0.86 (2)	1.95 (2)	2.809 (2)	176 (2)
N42—H42*B*⋯$O6^{vi}$	0.90 (2)	2.04 (2)	2.892 (2)	158 (2)
O1*W*—H1*W*⋯$O2W^{vii}$	0.84	1.91	2.746 (2)	176
O1*W*—H2*W*⋯O5	0.82 (3)	1.96 (3)	2.763 (2)	167 (3)
O2*W*—H3*W*⋯O6	0.90 (4)	1.82 (4)	2.707 (2)	171 (3)
O3*W*—H5*W*⋯O2*W*	0.96 (3)	1.86 (3)	2.804 (2)	170 (2)
C1—H1⋯O3*W*	0.99 (2)	2.57 (2)	3.544 (2)	168 (2)
C3—H13⋯O3*W*	0.93 (2)	2.60 (2)	3.208 (2)	123 (2)
C4—H14⋯$O1W^{i}$	0.95 (2)	2.69 (2)	3.611 (2)	163 (2)
C6—H16⋯$N11^{ii}$	0.95 (2)	2.66 (2)	3.450 (2)	141 (2)
C21—H21⋯$O1W^{iv}$	0.98 (2)	2.36 (2)	3.280 (2)	154 (2)
C31—H31⋯$O1^{iv}$	0.93 (2)	2.58 (2)	3.297 (2)	135 (2)
C51—H51⋯$O3^{iii}$	0.94 (2)	2.40 (2)	3.319 (2)	165 (2)
C61—H61⋯O2	0.90 (2)	2.53 (2)	3.397 (2)	162 (2)
C22—H22⋯$O3^{ii}$	0.94 (2)	2.65 (2)	3.376 (2)	135 (2)
C52—H52⋯$O6^{vi}$	0.96 (2)	2.58 (2)	3.304 (2)	132 (2)

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

Data collection

Kuma KM-4-CCD κ-geometry diffractometer with Sapphire CCD camera
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\rm min} = 0.894$, $T_{\rm max} = 0.984$
21075 measured reflections
6808 independent reflections
5206 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 1.06$
6808 reflections
282 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

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

P1—O1	1.5155 (8)	P2—O6	1.5350 (8)
P1—O2	1.5105 (9)	P2—C1	1.841 (1)
P1—O3	1.5817 (9)	N1—C1	1.475 (2)
P1—C1	1.832 (1)	N1—C2	1.385 (2)
P2—O4	1.5181 (8)	N2—C2	1.340 (2)
P2—O5	1.5284 (9)	N2—C6	1.354 (2)
O1—P1—O2	115.13 (4)	O4—P2—C1	107.38 (5)
O1—P1—O3	109.77 (5)	O5—P2—C1	108.17 (4)
O2—P1—O3	110.97 (4)	O6—P2—C1	104.50 (4)
O1—P1—C1	111.26 (4)	C1—N1—C2	121.58 (8)
O2—P1—C1	108.50 (4)	C1—N1—H2	113.1 (10)
O3—P1—C1	100.20 (4)	C2—N1—H2	112.6 (10)
O4—P2—O5	113.28 (4)	P1—C1—P2	116.39 (5)
O4—P2—O6	111.90 (5)	P1—C1—N1	109.34 (6)
O5—P2—O6	111.10 (4)	P2—C1—N1	110.46 (7)
O1—P1—C1—P2	57.76 (7)	O3—P1—C1—N1	−60.22 (7)
O2—P1—C1—P2	−69.88 (6)	O4—P2—C1—N1	−173.48 (6)
O3—P1—C1—P2	173.79 (5)	O5—P2—C1—N1	−50.90 (7)
O4—P2—C1—P1	−48.06 (6)	O6—P2—C1—N1	67.53 (7)
O5—P2—C1—P1	74.53 (6)	C2—N1—C1—P1	98.98 (9)
O6—P2—C1—P1	−167.04 (5)	C2—N1—C1—P2	−131.69 (8)
O1—P1—C1—N1	−176.25 (6)	C1—N1—C2—N2	34.58 (12)
O2—P1—C1—N1	56.11 (7)	C1—N1—C2—C3	−147.18 (9)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O6$^{\rm i}$	0.94 (2)	1.55 (2)	2.479 (1)	174 (2)
O1W—H1$W\cdots$O2	0.84 (2)	1.91 (2)	2.742 (2)	179 (2)
O1W—H2$W\cdots$O3$^{\rm ii}$	0.87 (2)	2.07 (2)	2.893 (2)	157 (2)
N1—H2$\cdots$O1W	0.86 (2)	2.49 (2)	3.315 (2)	160 (2)
N10—H1N$\cdots$O5	0.90 (2)	1.94 (2)	2.795 (2)	158 (2)
N10—H2N$\cdots$O1$^{\rm iii}$	0.88 (2)	2.07 (2)	2.927 (2)	165 (2)
N10—H3N$\cdots$O1$^{\rm ii}$	0.84 (2)	2.20 (2)	2.935 (2)	145 (2)
N10—H3N$\cdots$O4$^{\rm ii}$	0.84 (2)	2.36 (2)	2.970 (2)	130 (2)
N10—H4N$\cdots$O4$^{\rm iv}$	0.90 (2)	1.95 (2)	2.845 (2)	173 (2)
N20—H5N$\cdots$O1	0.89 (2)	2.60 (2)	3.085 (2)	115 (1)
N20—H5N$\cdots$O4	0.89 (2)	1.92 (2)	2.774 (2)	160 (2)
N20—H6N$\cdots$O5$^{\rm iv}$	0.89 (2)	2.05 (2)	2.927 (2)	172 (2)
N20—H7N$\cdots$O1$^{\rm iii}$	0.88 (2)	1.99 (2)	2.862 (2)	177 (2)
N20—H8N$\cdots$O2$^{\rm v}$	0.87 (2)	1.92 (2)	2.760 (2)	162 (2)
N30—H9N$\cdots$O6	0.88 (2)	1.83 (2)	2.700 (2)	169 (2)
N30—H10N$\cdots$N2	0.92 (2)	2.03 (2)	2.915 (2)	160 (2)
N30—H11N$\cdots$O5$^{\rm vi}$	0.90 (2)	1.86 (2)	2.750 (2)	169 (2)
N30—H12N$\cdots$O1$W^{\rm vii}$	0.86 (2)	2.13 (2)	2.894 (2)	149 (2)
C1—H1$\cdots$N2	0.98 (2)	2.44 (2)	2.892 (2)	108 (1)

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

Two of the three sites for water molecules in (I) are disordered. O2W was refined over two positions, with occupancies of 0.803 (5) and 0.197 (5) for O2W and O20W, respectively. Similarly, water molecule O3W, lying on a twofold axis, is occupationally disordered and refined to an occupancy of 0.803 (5). Owing to the low occupancy of O20W, only the O2W position is discussed. All of the non-H atoms were refined anisotropically, except for O20W. The positions of both H atoms on O20W and one of the H atoms on O2W have not been found. The remaining H atoms in (I) and (II) were found in difference Fourier maps and were refined isotropically, except for C7-bonded H atoms in (I), which were treated as riding atoms, with C—H distances of 0.98 Å and $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(C). Atom H1W in (I) was refined with the O—H distance restrained to 0.84 Å and with $U_{\rm iso}$(H) values set at $1.5U_{\rm eq}$(O1W).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2008); 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: TR3053). Services for accessing these data are described at the back of the journal.

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