Bis[(dihydrogen pyrophosphato-$\kappa^2 O,O'$)(2,2′:6′,2″-terpyridine-$\kappa^3 N,N',N''$)copper(II)] 4.5-hydrate

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metal-organic compounds

Bis[(dihydrogen pyrophosphato-κ²O,O')(2,2':6',2''-terpyridine-κ³N,N',N'')copper(II)] 4.5-hydrate

Mireille Perec[a] and Ricardo Baggio[b]*

[a]INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, UBA, Buenos Aires, Argentina, and [b]Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

The title copper complex, $[Cu(H_2P_2O_7)(C_{15}H_{11}N_3)]_2 \cdot 4.5H_2O$, consists of two very similar independent $Cu(Tpy)H_2P_2O_7$ monomeric units (Tpy is 2,2':6',2''-terpyridine) plus four and a half water molecules of hydration, some of which are disordered. Tpy units bind through the usual triple bite *via* their N atoms, and the $H_2P_2O_7{}^{2-}$ anions coordinate through two O atoms from two different phosphate units. Each independent CuN_3O_2 chromophore can be described as a slightly deformed square pyramid, with one of them having a sixth, semicoordinated, O atom from a centrosymmetrically related CuN_3O_2 unit in a weakly bound second apical position suggesting an octahedral environment for the cation and weak dimerization of the molecule. The two independent complex molecules are connected *via* two strong O—H···O interactions between the phosphate groups to form hydrogen-bonded dinuclear units, further linked into [111] columns, resulting in a very complex three-dimensional supramolecular structure through a variety of classical and nonclassical hydrogen bonds, as well as π–π interactions.

Comment

The pyrophosphate anion, $P_2O_7{}^{4-}$ or $[O_3P—O—PO_3]^{4-}$, plays a key role in biochemistry and in applied material sciences. Inorganic pyrophosphate materials are obtained *via* high-temperature solid-state precursor methods or hydrothermal techniques. It is an interesting ligand because of its multi-dentate nature, and can give rise to many different coordi-nation modes as it interacts with metal ions. In addition, it can be successively protonated to generate $HP_2O_7{}^{3-}$, $H_2P_2O_7{}^{2-}$ and $H_3P_2O_7{}^-$ anions, which may result in an additional large variety of structural topologies.

The susceptibility of the tetraanion to hydrolysis, particu-larly in the presence of M^{II} cations, has prevented the isolation of Cu^{II} metallo-organic pyrophosphate complexes for inves-tigation and the number of characterized structures remains limited. However, the use of chelating ligands in the synthetic
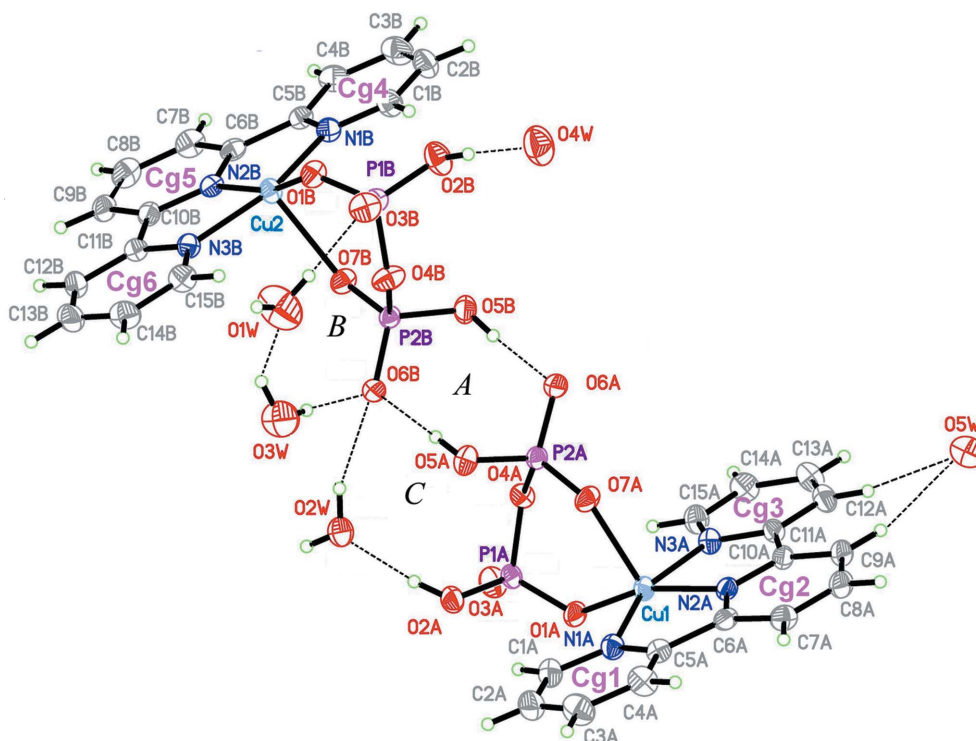

Figure 1
A molecular view of (I) (displacement ellipsoids are drawn at the 40% probability level), showing the atomic and centroid labelling, as well as the hydrogen bonds (dashed lines) providing dinuclear cohesion.

route and precise control of the factors influencing the synthetic process have recently allowed a number of Cu^{II} pyrophosphate coordination complexes to be isolated and investigated for their biological, magnetic and catalytic properties (Ikotun *et al.*, 2010). The Cu^{II} mononuclear pyrophosphate hydrate compounds H$_2$en[Cu$_2$(HP$_2$O$_7$)(en)(H$_2$O)]$_2$·2H$_2$O (en is ethylenediamine), (II) (Gharbi *et al.*, 1994), and {[(bipy)Cu(H$_2$O)(P$_2$O$_7$)Na$_2$(H$_2$O)$_6$]·4H$_2$O} (bipy is 2,2′-bipyridine), (III) (Doyle *et al.*, 2005), have been reported, with each Cu^{II} atom in a similar distorted square-pyramidal coordination geometry, but quite different geometries of the pyrophosphate groups. In order to further study the versatility and bonding of the pyrophosphate anion, we extend here the search into copper-based pyrophosphate systems with the tridentate 2,2′:6′,2″-terpyridine (Tpy) and report the preparation and crystal structure of the first Cu^{II} pyrophosphate with Tpy as coligand, *viz.* [Cu(Tpy)(H$_2$P$_2$O$_7$)]$_2$·4.5H$_2$O, (I), obtained from the reaction of Cu$_2$P$_2$O$_7$ and Tpy in phosphoric acid medium.

(I)
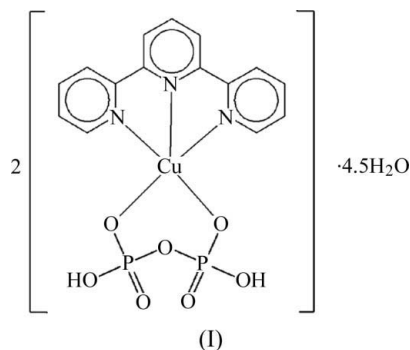
The asymmetric unit (Fig. 1) consists of two very similar independent Cu(Tpy)(P$_2$O$_7$H$_2$) monomeric units plus four and a half water molecules of hydration (see *Refinement* section for details on disorder). The Tpy units bind with their usual triple bite *via* the N atoms, and the H$_2$P$_2$O$_7^{2-}$ anions coordinate through two O atoms from different phosphate units (Table 1).

Each independent CuN$_3$O$_2$ chromophore can be described as a slightly deformed square pyramid [τ parameters, as defined in Addison *et al.* (1984): (161.81–158.67)/60 = 0.05 for unit *A* containing atom Cu1 and (163.48–159.45)/60 = 0.07 for unit *B* containing atom Cu2; see Fig. 1]. The polyhedra have one of the P$_2$O$_7$H$_2$ O atoms, O7 (*A/B*), at the apex with the remaining four atoms N1, N2, N3 and O1 (*A/B*) defining a roughly planar square base (in what follows, pairs of values correspond to complex molecules *A* and *B*, respectively): r.m.s. deviation from planarity = 0.0618 (3) and 0.0864 (5) Å; maximum deviation = 0.0718 (15) (N2*A*) and 0.1010 (14) Å (N2*B*); the copper cation is 0.2428 (13) and 0.1909 (13) Å above the plane towards the apices, which deviate by 6.01 (2) and 7.72 (2)° from the vertical. In unit *B*, the coordination description is complicated because of the presence of a semicoordinated O atom in a second apical position [Cu2···O1*B*^{ii} = 2.910 (2) Å; symmetry code: (ii) −x + 1, −y, −z + 1] which could allow the Cu2 environment to be described as octahedral. This interaction thereby weakly links two unit *B* molecules into centrosymmetric dimers.

A search of the Cambridge Structural Database (CSD, Version 5.3; Allen, 2002) disclosed a copper adenosine diphosphate complex [(adenosine 5′-diphosphato-*O*,*O*′)-(2,2′:6′,2″-terpyridine)copper(II)] (Cini & Pifferi, 1999) where the pyrophosphate (= diphosphate) anion is bound to a bulky adenosine group. The compound presents a very similar Cu + Tpy + P$_2$O$_7$ core as in (I), the copper environment being also square pyramidal with an identical N$_3$O basal plane and an apical O atom, and a comparable τ descriptor, 0.09 [0.05/0.07 for (I)]. The fact that the distortions imposed by the substituted anion lead to only slightly larger deformation of the polyhedron seems to indicate that the atomic disposition is fairly robust.

The independent Tpy units in (I) are, as expected, basically planar [r.m.s. deviation from planarity = 0.0332 (7) and 0.0413 (6) Å; maximum deviation = 0.065 (3) (C13*A*) and 0.073 (2) Å for (N2*B*)] and nearly parallel to each other [interplanar angle subtended = 6.11 (4)°]. The pyrophosphate anions are singly protonated at each phosphate end, balancing the Cu^{II} charges. As a result of chelation, three loops build up
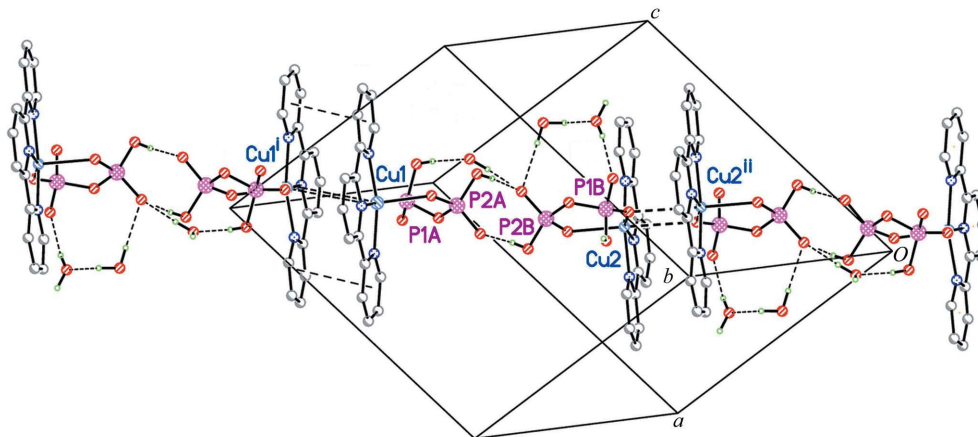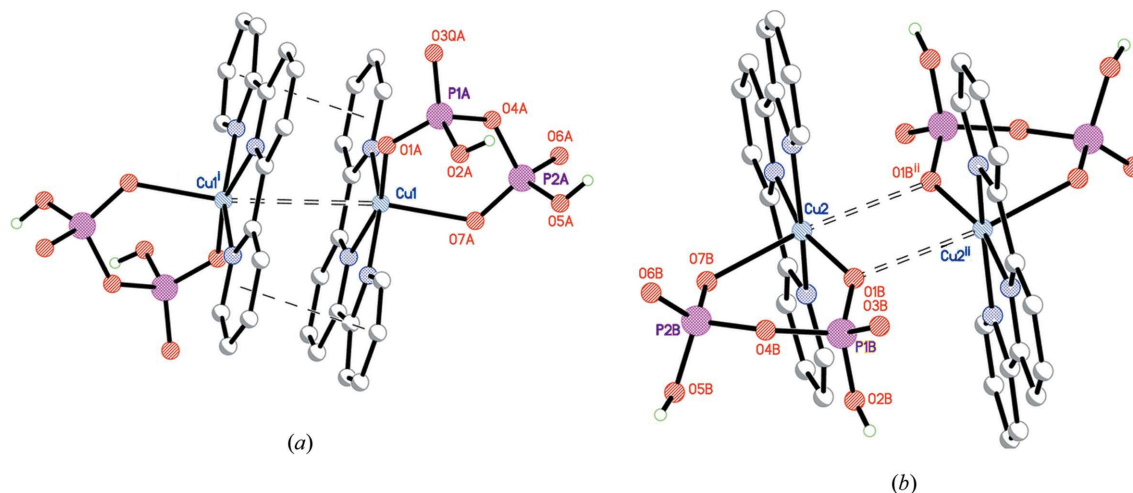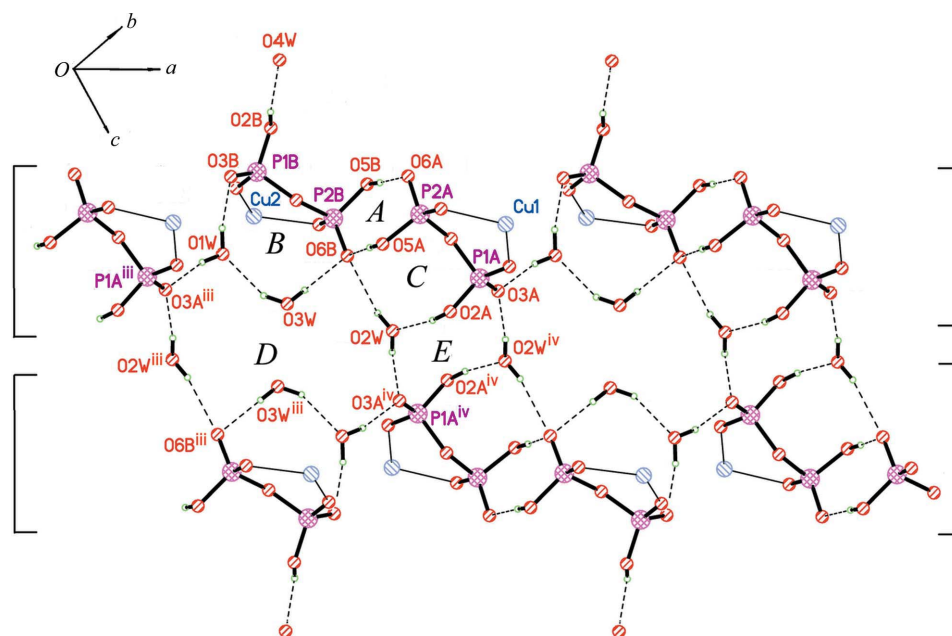

Figure 2
A view of the columnar motif chosen to describe the packing. [Symmetry codes: (i) −x + 2, −y + 1, −z + 2; (ii) −x + 1, −y, −z + 1.]

(a)

(b)

Figure 3
Details of the interactions between centrosymmetically related pairs of unit *A* and unit *B* molecules, which result in the columns presented in Fig. 2. (*a*) The dimer formed by two unit *A* molecules; single broken lines represent the π–π bonds responsible for the interaction and the double broken lines represent the Cu1$\cdots$Cu1$(-x + 2, -y + 1, -z + 2)$ short contact. (*b*) The dimer formed by two unit *B* molecules, with semicoordinative interactions shown by broken lines. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 2$; (ii) $-x + 1, -y, -z + 1$.]

Figure 4
Details of the intercolumnar interactions. Only copper cations, pyrophosphate anions and water molecules involved in hydrogen bonding have been drawn. Columns have been represented between square brackets, for clarity. Hydrogen bonds are shown as broken lines. [Symmetry codes: (iii) $x - 1, y, z$; (iv) $-x + 2, -y, -z + 2$.]

around each copper cation, *viz.* two smaller rings of the Cu—N—C—C—N– type, involving Tpy, and a much larger Cu—O—P—O—P—O– one mediated by the pyrophosphate group.

The two independent complex molecules interact with each other by way of two strong co-operative O—H$\cdots$O hydrogen bonds between adjacent dihydrogen pyrophosphate ligands (Table 2, entries 1–2). This defines a classical $R_2^2(8)$ ring [labelled *A* in Fig. 1; for graph-set notation, see Bernstein *et al.* (1995)], with *A* and *B* molecules connected into a non-centrosymmetric dinuclear unit. Inspection of Fig. 1 shows the way in which both phosphate anions are disposed at the centre of the group and the copper and Tpy units constituting the

limiting outermost ends (hereafter the Cu1 and Cu2 ends). Further linkage is achieved by hydrogen bonds mediated by the hydration water molecules O1*W*, O2*W* and O3*W* (Table 2, entries 3, 6, 8–10), which give rise to another two large rings with graph-set descriptors $R_3^3(10)$ and $R_3^2(10)$ (labelled *B* and *C*, respectively, in Fig. 1). Tables 2 (hydrogen bonding) and 3 (π–π interactions) give account of the profuse nonbonding interactions linking monomers in the crystal structure. The distribution of packing interactions is rather even in space, allowing many possible descriptions, from which we chose the one shown in Fig. 2. In this description, each dinuclear unit is connected head-to-head with its centrosymmetric images at

both Cu1 and Cu2 ends, to form columns parallel to [111]. At the Cu1 side, the interaction is basically π–π in nature (Fig. 3a and Table 3, first entry), connecting symmetry-related Tpy rings and bringing symmetry-related Cu1 centres close enough to be within an interacting distance (Table 1). The Cu2 end, in turn, connects with its symmetry-related image *via* a weak Cu2$\cdots$O1B^{ii} contact, leading to the formation of a closed four-membered loop (Table 1 and Fig. 3b).

Interconnection between columns is achieved *via* the collective action of the fully occupied site of the hydration water molecules O1W–O4W, which in addition to contributing to the dinuclear stability are crucial in the formation of the final three-dimensional structure (entries 5 and 7 in Table 2). In the process, they give rise to two types of centrosymmetric rings [graph-set codes $R_{10}^6(20)$ (D) and $R_4^4(12)$ (E)] threading a line of inversion centres along [100] (Fig. 4). Further linkage between columns is provided by a large number of weaker interactions, *viz*. nonclassical C—H$\cdots$O bonds having (C—H)$_{Tpy}$ as donors and phosphate O atoms as acceptors (entries 11–19 in Table 2) as well as extra π–π interactions between neighbouring Tpy groups, in addition to those involved in the column formation process already described (Table 3, entries 2–3).

In spite of its disordered nature (see *Refinement* section for details), the O4W$\cdots$O4W^x interaction [symmetry code: (x) $-x + 1, -y + 1, -z + 1$] effectively serves as a real link between the two centrosymmetrically related dinuclear units to which the water molecules are attached *via* Tpy. The O5W$\cdots$O7B^{viii} [symmetry code: (viii) $x, y + 1, z$] contact, by contrast, does not because of its 'terminal' character with no further interactions involving O5W.

There are few copper pyrophosphates reported in the literature (ten entries in Version 5.32 of the CSD; Allen, 2002) and only two of them are mononuclear [compounds (II) and (III) mentioned above]. In the mononuclear coordination compounds (I), (II) and (III) the pyrophosphate ligands show different degrees of protonation, *viz*. H$_2$P$_2$O$_7{}^{2-}$ in (I), HP$_2$O$_7{}^{3-}$ in (II) and P$_2$O$_7{}^{4-}$ in (III), depending upon reaction conditions. As a result (I) is a neutral complex, (II) is ionic (with complex units presenting a single negative charge balanced by H$_2$en^{2+} counter-ions) and (III) presents a centrosymmetric 'zwitterionic' structure with a central [Na$_4$(H$_2$O)$_{12}$]$^{4+}$ core, to which two (2−) complex units attach at each side to produce a neutral cluster. Also, the way in which individual phosphate groups dispose relative to one another upon chelation is notably different: in compound (II) they bind in an almost eclipsed geometry, with an O—P$\cdots$P—O torsion angle of 4.9 (1)° (where O represents the coordinated O atom); in (III), instead, the groups appear almost staggered [O—P$\cdots$P—O = 51.0 (1)°]; while (I) presents an intermediate position, with equivalent torsion angles of 15.6 (1) and 15.9 (1)° for units A and B, respectively.

Experimental

Cu$_2$P$_2$O$_7$ (0.26 g, 1 mmol) was added to an alcohol–water (50 ml, 1:1 v:v) solution containing 2,2′:6′,2″-terpyridine (0.26 g, 1 mmol) and the resulting solution stirred for 4 h at room temperature. A few drops of concentrated phosphoric acid (85%) was added to clear the solution which was then filtered. After two weeks, green crystals were separated and dried in air. Analysis calculated for C$_{30}$H$_{26}$Cu$_2$N$_6$-O$_{14}$P$_4$·4.5H$_2$O: C 35.06, H 3.44, N 8.18%; found: C 35.15, H 3.45, N 8.22%. Yield based on Cu$_2$P$_2$O$_7$: 55%.

Table 1
Selected interatomic distances (Å).

Cu1—O1A	1.918 (2)	Cu2—O1B	1.927 (2)
Cu1—N2A	1.932 (3)	Cu2—N2B	1.940 (3)
Cu1—N1A	2.039 (3)	Cu2—N1B	2.032 (3)
Cu1—N3A	2.046 (3)	Cu2—N3B	2.043 (3)
Cu1—O7A	2.206 (2)	Cu2—O7B	2.298 (2)
Cu1$\cdots$Cu1^i	3.7720 (8)	Cu2$\cdots$O1B^{ii}	2.910 (2)
Cu2$\cdots$Cu2^{ii}	3.6977 (8)		

Symmetry codes: (i) $-x + 2, -y + 1, -z + 2$; (ii) $-x + 1, -y, -z + 1$.

Two hydration water molecules (O4W and O5W) present positional disorder of different kinds, leading to some apparently odd short contacts, but easily accountable for when disorder is taken into account. O5W is only partially occupied, with an occupancy factor that refined to a value slightly larger than 0.5. In its final position, the O atom 'bumps' its O5W^{xi} [symmetry code: (xi) $-x + 2, -y + 2, -z + 1$] centrosymmetric image 1.830 (1) Å away, so they cannot be but mutually exclusive and the corresponding occupancy factor was accordingly fixed at 0.50. There is, in addition, a short O5W$\cdots$O7B^{viii} [symmetry code: (viii) $x, y + 1, z$] distance of 2.870 (4) Å, which can in principle be explained by a hydrogen bond donated by the partial-occupancy O5W water molecule and accepted by the pyrophosphate anion. On the other hand, O4W is fully occupied, but rather near [2.839 (4) Å] the inversion-related O4W^x [symmetry code: (x) $-x + 1, -y + 1, -z + 1$], a fact only accountable for through hydrogen bonding but inconsistent with an inversion centre between the two identical moieties. In addition, no clear H-atom images could be

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O5A-H5A\cdots O6B$	0.85 (2)	1.83 (2)	2.672 (3)	174 (4)
$O5B-H5B\cdots O6A$	0.85 (2)	1.75 (2)	2.601 (3)	175 (2)
$O2A-H2A\cdots O2W$	0.84 (3)	1.76 (3)	2.591 (4)	171 (3)
$O2B-H2B\cdots O4W$	0.85 (2)	1.86 (2)	2.716 (4)	175 (3)
$O1W-H1WA\cdots O3A^{iii}$	0.84 (3)	1.88 (3)	2.709 (5)	167 (4)
$O1W-H1WB\cdots O3B$	0.84 (3)	1.87 (3)	2.656 (5)	156 (5)
$O2W-H2WA\cdots O3A^{iv}$	0.85 (3)	1.88 (3)	2.716 (4)	172 (3)
$O2W-H2WB\cdots O6B$	0.85 (3)	2.10 (3)	2.883 (4)	153 (4)
$O3W-H3WA\cdots O1W$	0.85 (4)	2.02 (4)	2.687 (5)	136 (3)
$O3W-H3WB\cdots O6B$	0.85 (3)	2.04 (3)	2.885 (4)	177 (5)
$C1B-H1B\cdots O2B$	0.93	2.45	3.360 (5)	165
$C4B-H4B\cdots O4A^{v}$	0.93	2.53	3.409 (5)	158
$C9B-H9B\cdots O7A^{vi}$	0.93	2.40	3.280 (5)	157
$C15B-H15B\cdots O1W$	0.93	2.57	3.430 (7)	154
$C7A-H7A\cdots O3W^{vii}$	0.93	2.54	3.469 (5)	173
$C8A-H8A\cdots O6B^{viii}$	0.93	2.48	3.407 (5)	177
$C9A-H9A\cdots O5W$	0.93	2.40	3.319 (7)	169
$C12A-H12A\cdots O5W$	0.93	2.57	3.478 (8)	164
$C14A-H14A\cdots O3B^{ix}$	0.93	2.51	3.355 (5)	151

Symmetry codes: (iii) $x-1, y, z$; (iv) $-x+2, -y, -z+2$; (v) $-x+2, -y, -z+1$; (vi) $x, y-1, z$; (vii) $-x+1, -y+1, -z+2$; (viii) $x, y+1, z$; (ix) $x+1, y, z$.

Table 3
$\pi-\pi$ interactions (Å, °) for (I).

Centroids are as defined in Fig. 1; c.c.d. is the distance between ring centroids, i.p.d. is the mean perpendicular distance from one plane to the neighbouring centroid and s.a. is the mean angle subtended by the intercentroid vector to the plane normal. For details, see Janiak (2000).

Group 1/group 2	c.c.d. (Å)	i.p.d. (Å)	s.a. (°)
$Cg1/Cg3^{i}$	3.629 (2)	3.39 (2)	20.7 (1.0)
$Cg2/Cg6^{vi}$	3.674 (2)	3.34 (1)	24.4 (3)
$Cg3/Cg5^{vi}$	4.159 (2)	3.42 (4)	34.7 (1.0)

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (vi) $x, y-1, z$.

found in the difference map, for which rotational disorder is to be assumed. This disordered model would allow for the possibility of hydrogen-bonding interaction between the two neighbours, while permitting an 'average' inversion operation which would apply 'truly' only for the O atoms but not to the H₂O groups as a whole. This is not unusual in water solvates built up around a symmetry centre. All the H atoms in the structure (except those corresponding to the disor-

dered water molecules O4W and O5W) could be located in a difference Fourier map; those attached to O atoms were further refined with restraints [for water molecules: $O-H = 0.85$ (1) Å and $H\cdots H = 1.35$ (2) Å; for phosphate groups: $O-H = 0.85$ (1) Å and $P\cdots H = 2.05$ (2) Å]. H atoms attached to C atoms were placed at calculated positions ($C-H = 0.93$ Å) and allowed to ride. In all cases, displacement parameters were taken as $U_{iso}(H) = 1.2U_{eq}$(host).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; 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: *SHELXTL* and *PLATON* (Spek, 2009).

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