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Hexakis(melaminium) tetrakis(dihydrogenphosphate) monohydrogenphosphate tetrahydrate

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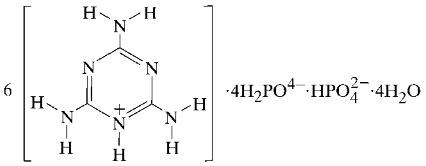
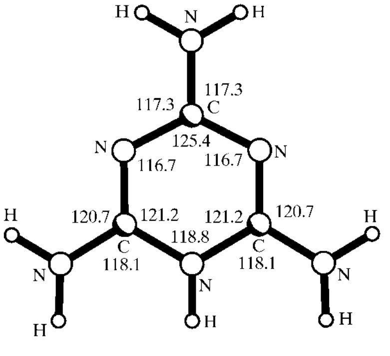
The crystal structure of the new melaminium salt, hexakis(2,4,6-triamino-1,3,5-triazin-1-ium) tetrakis(dihydrogenphosphate) monohydrogenphosphate tetrahydrate, $6C_3H_7N_6^+\cdot 4H_2PO_4^-\cdot HPO_4^{2-}\cdot 4H_2O$, is built up from singly protonated melaminium residues, dihydrogenphosphate and monohydrogenphosphate anions, and water molecules. The melaminium residues are interconnected by four N—H···N hydrogen bonds, forming chains along the [001] direction. These chains of melaminium residues form stacks aligned along [100]. The dihydrogenphosphate anions interact with the monohydrogenphosphate anions *via* the H atoms and, together with hydrogen-bonded dimers of the water molecules, develop layers parallel to the (010) plane. The oppositely charged moieties interact *via* multiple N—H···O hydrogen bonds that stabilize the stacking structure.

Comment

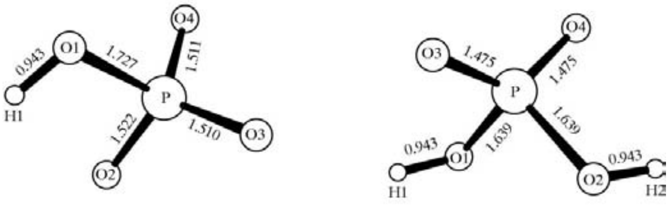
The present study is a continuation of our investigation of the hydrogen bonds formed by melamine in the solid state (Janczak & Perpétuo, 2001*a*,*b*,*c*,*d*; Perpétuo & Janczak, 2002). Melamine and its organic and inorganic complexes or salts can develop supramolecular structures *via* multiple hydrogen bonds through self-assembly of components which contain complementary arrays of hydrogen-bonding sites (MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). As part of a study of the solid-state properties of these compounds, we report here the structure of the title compound, (I).



Crystals of melaminium selenate exhibit second-harmonic generation (SHG) with about 40% efficiency (Marchewka *et al.*, 2002). Compound (I) is being studied as a potential material for non-linear optics since, like the selenate salt, it crystallizes in a non-centrosymmetric space group. Additionally, the X-ray geometry of (I) is compared here with the *ab initio* fully optimized parameters calculated at the HF/6-31G(*d*,*p*) level (Frisch *et al.*, 1995). The *ab initio* molecular-orbital calculations were carried out on the isolated ions, *i.e.* the monoprotonated melaminium cation and the phosphate $H_2PO_4^-$ and HPO_4^{2-} anions, and the results are illustrated in Schemes 1 and 2, where values are given in Å and in °.



Scheme 1



O1—P—O2	99.20
O1—P—O3	104.69
O1—P—O4	104.68
O2—P—O3	115.20
O2—P—O4	104.69
O3—P—O4	115.22

O1—P—O2	109.94
O1—P—O3	106.05
O1—P—O4	108.21
O2—P—O3	106.05
O2—P—O4	106.05
O3—P—O4	124.88

Scheme 2

The asymmetric unit of (I) consists of six melaminium residues, each protonated at one ring N atom, four dihydrogenphosphate anions, $H_2PO_4^-$, one monohydrogenphosphate anion, HPO_4^{2-}, and four water molecules (Fig. 1). The six independent melaminium cations do not differ significantly, but the six-membered aromatic rings exhibit significant distortions from the ideal hexagonal form. In all the melaminium residues, the internal C—N—C angle at the protonated N atom (N11, N21, N31, N41, N51 and N61) is significantly greater (mean 119.4°) than the other two C—N—C angles within the ring (mean 115.9°). This is a result of the steric effect of a lone-pair electron, predicted by the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992).

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As a result of the protonation of the melamine ring at one ring N atom (N11, N21, N31, N41, N51 and N61), the internal N—C—N angles containing only non-protonated N atoms (mean 125.5°) are significantly greater than the N—C—N angles containing both protonated and non-protonated N atoms (mean 121.5°). The correlation between the internal C—N—C angles within the melaminium rings is similar to those reported for the crystals of barbituric acid with melamine (Zerkowski *et al.*, 1994), melaminium phthalate (Janczak & Perpétuo, 2001*a*), melaminium chloride hemihydrate (Janczak & Perpétuo, 2001*c*), bis(melaminium) sulfate dihydrate (Janczak & Perpétuo, 2001*d*) and melaminium acetate monohydrate acetic acid solvate (Perpétuo & Janczak, 2002), *i.e.* those singly protonated melaminium salts that have been previously structurally characterized. The *ab initio* optimized geometry calculated at the HF/6-31G(*d*,*p*) level (Frisch *et al.*, 1995) on the singly protonated melaminium residue (Scheme 1) shows a similar correlation between the C—N—C and N—C—N angles within the ring to that in the crystal. Thus, the ring distortion of singly protonated melaminium residues results mainly from the protonation, and, to a lesser degree, from the hydrogen-bonding system and the crystal packing.

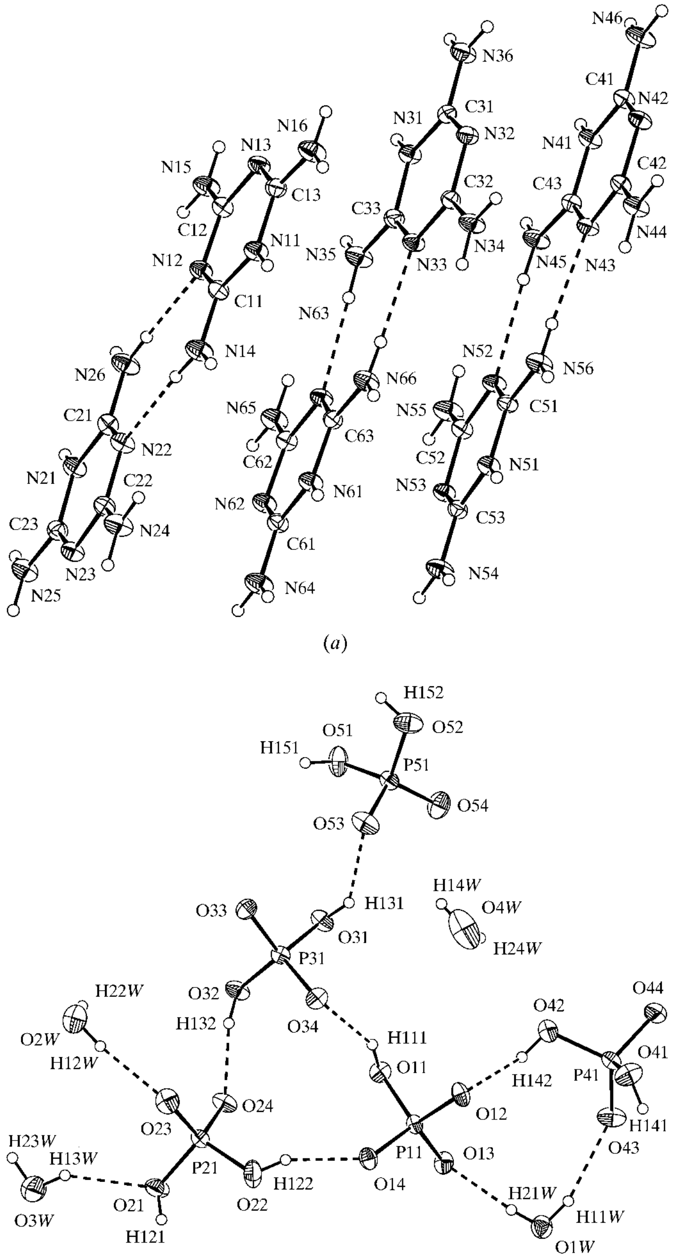


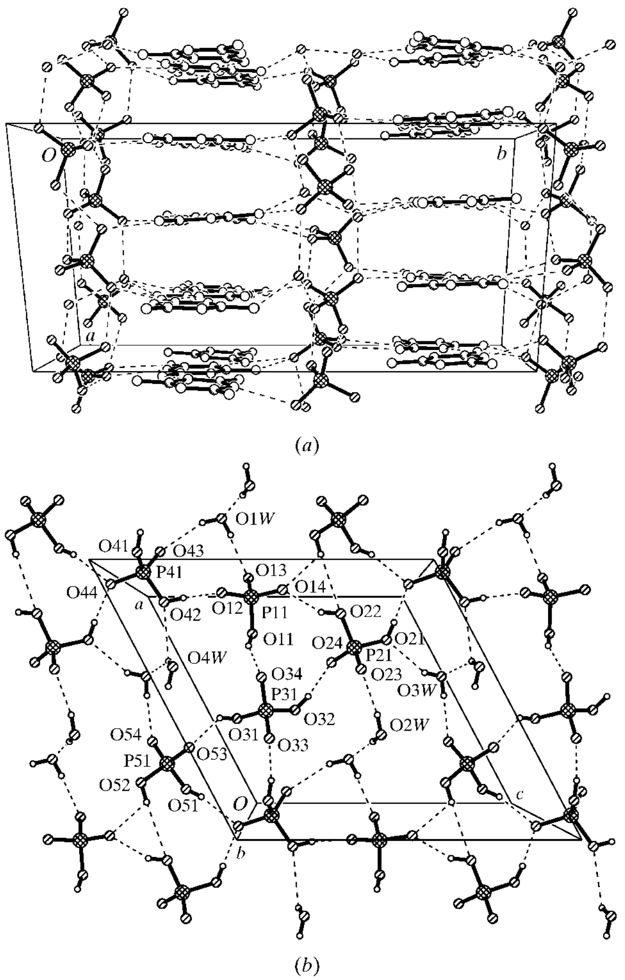
Figure 1
The molecular structure of (I) showing (*a*) the melaminium cations and (*b*) the phosphate anions and water molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Each melaminium residue in the crystal of (I) is involved in nine hydrogen bonds, in seven of them as donor H and in the remaining two as acceptor H. The four almost linear N—H···N bonds link the melaminium residue with two neighbouring melaminium residues, forming a chain along the [001] direction (Fig. 2*a*), while the remaining five much more bent N—H···O bonds link chains of melaminium residues with phosphate anions and/or a water molecule. The melaminium residue *M*1 (containing atoms N11, N12, N13, N14, N15, N16, C11, C12 and C13; the first number is the number of the melaminium residue and the second is the atom number) is involved in N—H···O hydrogen bonds with a water molecule (O2*W*), the monohydrogenphosphate anion (O11) and two different dihydrogenphosphate anions, forming two hydrogen bonds with one of them (O21 and O24). The melaminium residues *M*2 and *M*3 are involved in N—H···O hydrogen bonds with two water molcules, *M*2 with O2*W* and O3*W*, and *M*3 with O1*W* and O4*W*. Additionally, residue *M*2 links two $H_2PO_4^-$ and one HPO_4^{2-} anion, while residue *M*3 is involved in N—H···O hydrogen bonds with three different $H_2PO_4^-$ anions. Residues *M*4 and *M*5 do not form any hydrogen bonds with water molecules. Residue *M*4 forms N—H···O hydrogen bonds with two different $H_2PO_4^-$ anions and with two HPO_4^{2-} anions, forming two hydrogen bonds to one of them. Residue *M*6 forms hydrogen bonds with a water molecule (O4*W*) and with three different $H_2PO_4^-$ anions, forming two hydrogen bonds with one of them (atoms O31 and O32 of the same $H_2PO_4^-$ anion).

The geometries of the four independent dihydrogenphosphate anions, $H_2PO_4^-$, do not differ significantly, with the two single P—OH bonds ranging from 1.545 (2) to 1.569 (2) Å, and the other two P—O bonds ranging from 1.485 (2) to 1.524 (2) Å. These values correlate well with those observed in the crystals of other compounds containing the dihydrogenphosphate anion (Allen *et al.*, 1987), but they differ from the optimized bond lengths calculated for the dihydrogenphosphate anion. The greatest differences are observed between the values of the O—P—O angle containing both non-protonated O atoms and in the P—OH bond lengths (see Scheme 2). The optimized O—P—O angle in the $H_2PO_4^-$ anion is about 10° greater than those in the crystal, and can be explained by the steric effect of the three lone pairs of electrons on both non-protonated O atoms. The observed P—OH bond lengths in the crystal are shorter than the optimized values, which is likely to be due to the intermolecular interactions present in the crystal, since the calculated values refer to the isolated non-interacting $H_2PO_4^-$ anion. The X-ray geometry of the monohydrogenphosphate anion, HPO_4^{2-}, differs slightly from the optimized results (Scheme 2). In particular, the single P—OH bond is significantly longer (0.145 Å) in the optimized HPO_4^{2-} anion than in the crystal. The differences in the P—O distances for equivalent bonds in the $H_2PO_4^-$ and HPO_4^{2-} anions correlate with the number and strength of the hydrogen bonds in which the O atoms are involved (Table 2).

The monohydrogenphosphate anion, HPO_4^{2-}, is involved in nine hydrogen bonds, in eight of them as acceptor H and in one as donor H. The HPO_4^{2-} anion forms hydrogen bonds as acceptor H with four melaminium residues *via* their amine H atoms, forming two hydrogen bonds with one melaminium residue (*via* an amine H atom and the H atom at the protonated ring N atom), and with two $H_2PO_4^-$ anions, and acts as a donor H to atom O34 of one $H_2PO_4^-$ anion.

Each of the four independent $H_2PO_4^-$ anions is involved in nine hydrogen bonds, in seven as acceptor H and in two as donor H. The dihydrogenphosphate anion containing atom P21 forms hydrogen bonds with four different melaminium residues, forming two hydrogen bonds with one of them *via* an amine H atom and the H atom at the protonated ring N atom, and with two other $H_2PO_4^-$ anions (containing P31 and P41), a monohydrogenphosphate anion (HPO_4^{2-}) and two water molecules (O2*W* and O3*W*). The P21—O24 bond is longer than P21—O23 (both bonds chemically equivalent), since atom O24 acts as acceptor H in two stronger hydrogen bonds than atom O23. The $H_2PO_4^-$ anion containing atom P31 is involved as acceptor H with four melaminium residues (forming two hydrogen bonds with one), three different $H_2PO_4^-$ anions and the HPO_4^{2-} anion, and does not form hydrogen bonds with water molecules. The $H_2PO_4^-$ anion containing atom P41 is involved as acceptor H with three melaminium residues (forming two hydrogen bonds with one), two $H_2PO_4^-$ anions and one water molecule (O1*W*), and as donor H with $H_2PO_4^-$ and HPO_4^{2-} anions. The $H_2PO_4^-$ anion containing atom P51 as acceptor H forms hydrogen bonds with four different melaminium residues, one water molecule (O3*W*) and one $H_2PO_4^-$ ion (containing atom P31), and as donor H, it forms hydrogen bonds with $H_2PO_4^-$ (containing atom P41) and the HPO_4^{2-} anion.



(*a*)

(*b*)

Figure 2

The crystal packing of (I), showing (*a*) the stacking structure, where the dashed lines represent hydrogen bonds and H atoms have been omitted for clarity, and (*b*) the layer of hydrogen-bonded dihydrogenphosphate and monohydrogenphosphate anions with the hydrogen-bonded dimeric structure of the water molecules. The layer in (*b*) is parallel to the (010) plane.

The water molecules form hydrogen-bonded dimeric structures, with O2*W*—H22*W*···O1*W*($x - 1, y, z$) = 2.825 (2) and O4*W*—H24*W*···O3*W*($x, y, z - 1$) = 2.863 (2) Å. This hydrogen-bonded dimeric structure of the water molecules forms a two-dimensional layer, parallel to the (010) plane, with the mono- and dihydrogenphosphate anions, *via* O—H···O hydrogen bonds (Fig. 2*b*).

In the crystal of (I), the melaminium residues form planar positively charged chains, interconnected by complementary N—H···N bonds, forming stacks parallel to the (010) plane (Fig. 2*a*). The hydrogen-bonded dihydrogenphosphate and monohydrogenphosphate anions are interconnected by water molecules, forming negatively charged layers that are located in the crystal parallel to the (010) plane. Both oppositely charged moieties are extensively interconnected by multiple hydrogen bonds that stabilize the structure (Fig. 2*a*). Full details of the hydrogen-bonding geometry are given in Table 2.

Experimental

Melanine was dissolved in a 20% solution of phosphoric acid and the resulting solution was slowly evaporated. After several days, colourless crystals of the title salt, (I), appeared.

Crystal data

$6C_3H_7N_6^+ \cdot 4H_2PO_4^- \cdot HPO_4^{2-} \cdot 4H_2O$
M_r = 1318.86
Monoclinic, $P2_1$
a = 11.341 (2) Å
b = 20.965 (4) Å
c = 12.334 (2) Å
β = 117.80 (3)°
V = 2594.1 (11) Å^3
Z = 2
D_x = 1.689 Mg m^{-3}
D_m = 1.69 Mg m^{-3}
D_m measured by flotation in 1,2-dichloroethane/1,2-dibromoethane
Mo $K\alpha$ radiation
Cell parameters from 4999 reflections
θ = 2.7–29°
μ = 0.29 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.32 × 0.28 × 0.25 mm

Data collection

Kuma KM-4 diffractometer with a two dimensional CCD area-detector
ω scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.913$, $T_{\max} = 0.931$
25 398 measured reflections
12 689 independent reflections
10 664 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 29.1°$
$h = -15 \rightarrow 10$
$k = -28 \rightarrow 28$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.067$
$S = 1.00$
12 689 reflections
773 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.2410P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00059 (12)
Absolute structure: Flack (1983), 6821 Friedel pairs
Flack parameter = 0.11 (4)

Table 1
Selected geometric parameters (Å, °).

P11—O13	1.4969 (13)	P31—O32	1.5588 (12)
P11—O14	1.5261 (12)	P31—O31	1.5688 (12)
P11—O12	1.5357 (12)	P41—O43	1.4929 (14)
P11—O11	1.5832 (14)	P41—O44	1.5239 (15)
P21—O23	1.4985 (15)	P41—O42	1.5454 (14)
P21—O24	1.5101 (13)	P41—O41	1.5571 (14)
P21—O21	1.5569 (14)	P51—O54	1.4854 (15)
P21—O22	1.5672 (15)	P51—O53	1.5093 (15)
P31—O33	1.5030 (13)	P51—O52	1.5605 (15)
P31—O34	1.5098 (14)	P51—O51	1.5787 (14)
O13—P11—O14	113.09 (8)	O33—P31—O31	108.85 (8)
O13—P11—O12	112.97 (7)	O34—P31—O31	111.16 (8)
O14—P11—O12	108.41 (7)	O32—P31—O31	101.65 (7)
O13—P11—O11	106.01 (7)	O43—P41—O44	112.55 (9)
O14—P11—O11	108.10 (7)	O43—P41—O42	112.72 (9)
O12—P11—O11	108.01 (8)	O44—P41—O42	107.62 (9)
O23—P21—O24	114.09 (8)	O43—P41—O41	110.71 (8)
O23—P21—O21	109.71 (9)	O44—P41—O41	108.10 (9)
O24—P21—O21	107.71 (8)	O42—P41—O41	104.75 (9)
O23—P21—O22	108.84 (9)	O54—P51—O53	115.14 (10)
O24—P21—O22	110.41 (8)	O54—P51—O52	113.39 (9)
O21—P21—O22	105.75 (9)	O53—P51—O52	103.77 (8)
O33—P31—O34	112.99 (7)	O54—P51—O51	104.65 (8)
O33—P31—O32	111.26 (8)	O53—P51—O51	111.76 (9)
O34—P31—O32	110.36 (8)	O52—P51—O51	108.11 (9)

All H atoms were located from difference Fourier maps. In the final refinement, H atoms bonded to the N atoms of the melamine residues were treated as riding, with N—H = 0.86 Å; the H atoms of the phosphate anions were constrained, with O—H = 0.82 Å. The H atoms of the water molecules were refined and the resulting range of O—H distances was 0.78 (2)–0.86 (2) Å.

Data collection: *KM*-4 *CCD Software* (Kuma Diffraction, 2000); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H111···O34	0.82	1.896	2.648 (2)	152
O21—H121···O44$^{\rm i}$	0.82	1.779	2.490 (2)	144
O22—H122···O14	0.82	1.829	2.580 (2)	152
O31—H131···O53	0.82	1.921	2.599 (2)	139
O32—H132···O24	0.82	1.766	2.502 (2)	148
O41—H141···O33$^{\rm ii}$	0.82	1.742	2.529 (2)	160
O42—H142···O12	0.82	1.843	2.533 (2)	141
O51—H151···O44$^{\rm iii}$	0.82	1.963	2.683 (2)	146
O52—H152···O14$^{\rm iv}$	0.82	2.161	2.594 (2)	113
N11—H11···O24$^{\rm v}$	0.86	1.824	2.661 (2)	164
N14—H14*A*···N22	0.86	2.115	2.974 (2)	177
N14—H14*B*···O11$^{\rm v}$	0.86	2.290	2.987 (2)	138
N15—H15*A*···O33	0.86	2.046	2.888 (2)	166
N15—H15*B*···O2*W*	0.86	2.078	2.886 (2)	156
N16—H16*A*···N23$^{\rm vi}$	0.86	2.186	3.043 (2)	174
N16—H16*B*···O21$^{\rm v}$	0.86	2.192	3.024 (2)	163
N21—H21···O53$^{\rm i}$	0.86	2.034	2.869 (2)	164
N24—H24*A*···O11$^{\rm v}$	0.86	2.432	3.261 (2)	162
N24—H24*B*···O3*W*$^{\rm vii}$	0.86	2.165	2.909 (2)	145
N25—H25*A*···N13$^{\rm i}$	0.86	2.133	2.991 (2)	175
N25—H25*B*···O33$^{\rm i}$	0.86	2.203	2.840 (2)	131
N26—H26*A*···N12	0.86	2.137	2.997 (2)	178
N26—H26*B*···O2*W*	0.86	2.251	2.857 (2)	127
N31—H31···O34	0.86	1.849	2.699 (2)	169
N34—H34*A*···O54$^{\rm viii}$	0.86	2.034	2.879 (2)	167
N34—H34*B*···O1*W*$^{\rm ix}$	0.86	2.085	2.861 (2)	150
N35—H35*A*···N63	0.86	2.109	2.968 (2)	178
N35—H35*B*···O23	0.86	2.072	2.750 (2)	135
N36—H36*A*···N62$^{\rm vi}$	0.86	2.163	3.022 (2)	178
N36—H36*B*···O4*W*	0.86	2.145	2.779 (2)	130
N41—H41···O12	0.86	1.845	2.693 (2)	168
N44—H44*A*···O13$^{\rm ix}$	0.86	2.071	2.920 (2)	169
N44—H44*B*···O51$^{\rm viii}$	0.86	2.366	3.148 (2)	151
N45—H45*A*···N52	0.86	2.188	3.047 (2)	177
N45—H45*B*···O14	0.86	2.000	2.859 (2)	178
N46—H46*A*···N53$^{\rm vi}$	0.86	2.082	2.936 (2)	172
N46—H46*B*···O41	0.86	2.402	2.986 (2)	126
N51—H51···O43$^{\rm ix}$	0.86	1.788	2.623 (2)	163
N54—H54*A*···N42$^{\rm i}$	0.86	2.173	3.031 (2)	176
N54—H54*B*···O44$^{\rm ix}$	0.86	2.313	3.128 (2)	158
N55—H55*A*···O41$^{\rm i}$	0.86	2.304	3.100 (2)	154
N55—H55*B*···O22	0.86	2.292	2.996 (2)	139
N56—H56*A*···N43	0.86	2.096	2.953 (2)	174
N56—H56*B*···O13$^{\rm ix}$	0.86	2.105	2.768 (2)	134
N61—H61···O31$^{\rm v}$	0.86	2.064	2.914 (2)	169
N64—H64*A*···N32$^{\rm i}$	0.86	2.109	2.968 (2)	177
N64—H64*B*···O54$^{\rm v}$	0.86	2.293	2.925 (2)	130
N65—H65*A*···O4*W*$^{\rm i}$	0.86	2.106	2.958 (2)	171
N65—H65*B*···O23	0.86	2.142	2.983 (3)	166
N66—H66*A*···N33	0.86	2.146	3.006 (2)	178
N66—H66*B*···O32$^{\rm v}$	0.86	2.058	2.880 (2)	160
O1*W*—H11*W*···O43	0.82 (2)	2.18 (2)	2.941 (2)	154 (2)
O1*W*—H21*W*···O13	0.78 (2)	1.97 (2)	2.728 (2)	166 (2)
O2*W*—H12*W*···O23	0.82 (2)	1.96 (2)	2.763 (2)	166 (2)
O2*W*—H22*W*···O1*W*$^{\rm iii}$	0.85 (2)	1.98 (2)	2.825 (2)	173 (2)
O3*W*—H13*W*···O21	0.86 (2)	2.09 (2)	2.835 (2)	145 (2)
O3*W*—H23*W*···O54$^{\rm i}$	0.85 (2)	1.96 (2)	2.741 (2)	153 (2)
O4*W*—H24*W*···O3*W*$^{\rm vi}$	0.80 (2)	2.17 (2)	2.863 (2)	145 (2)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1207). Services for accessing these data are described at the back of the journal.

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