

Zhanhui Yuan and William  
Clegg\*School of Natural Sciences (Chemistry),  
University of Newcastle upon Tyne,  
Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

## Key indicators

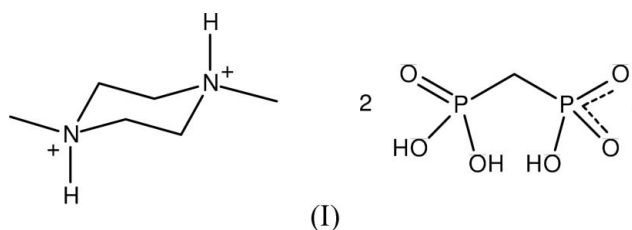
Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å  
 $R$  factor = 0.028  
 $wR$  factor = 0.075  
Data-to-parameter ratio = 15.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.*N,N'*-Dimethylpiperazinium(2+)  
bis[methylenehydrogendiphosphonate(1-)]

The asymmetric unit of the title compound,  $\text{C}_6\text{H}_{16}\text{N}_2^{2+} \cdot 2(\text{HO})_2(\text{O})\text{PCH}_2\text{P}(\text{O})_2(\text{OH})^-$ , contains two singly charged diphosphonate anions and two half-cations, each doubly charged cation lying on an inversion centre. Single deprotonation of methylenediphosphonic acid to give a salt with an organic amine is unprecedented, double deprotonation being normal. All N—H and O—H groups act as hydrogen-bond donors in the crystal structure, with unprotonated O atoms as the acceptors, giving a three-dimensional network.

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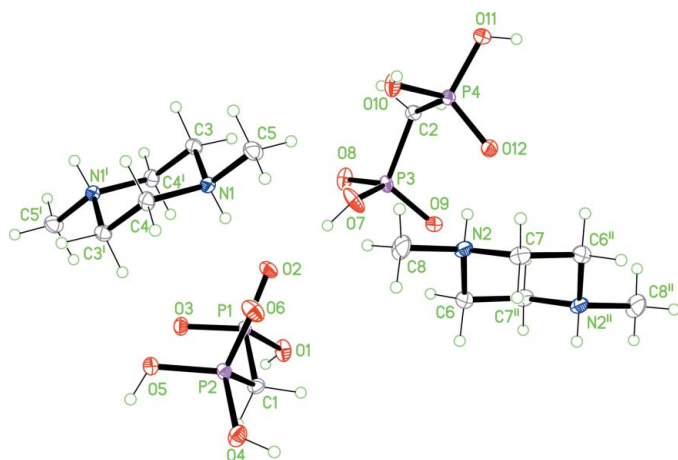
## Comment

Phosphonic and diphosphonic acids are extremely versatile building blocks in supramolecular chemistry (Farrell *et al.*, 2001; Ferguson *et al.*, 1998; Glidewell *et al.*, 2000; Wheatley *et al.*, 2001). An important factor in the behaviour of such acids is the marked difference in acidity for stepwise deprotonation of the two hydroxyl functions in each  $-\text{PO}(\text{OH})_2$  group. With organic amines, typically only one proton per phosphonate group is transferred from O to N. The resulting  $-\text{P}(\text{O})_2(\text{OH})-$  group can thus act as a hydrogen-bond donor as well as an acceptor. The structure of methyldiphosphonic acid itself (DeLaMatter *et al.*, 1973) consists of a three-dimensional hydrogen-bonded network.



The title compound, (I), obtained unintentionally in one of a series of hydrothermal syntheses of aluminium diphosphonate complexes, is a 1:2 salt of diprotonated piperazine (generated by coupling of trimethylamine under the hydrothermal conditions) and the singly charged anion of methylenediphosphonic acid obtained by removal of only one proton; the second phosphonic acid group remains uncharged. Although there appears to be no previous report of such a reaction of trimethylamine to produce *N,N'*-dimethylpiperazine, this product can be obtained from trimethylamine oxide by deprotonation (Beugelmans *et al.*, 1985).

The asymmetric unit of (I) contains two anions and two half-cations, each cation lying on an inversion centre (Fig. 1). Both independent piperazine rings have the expected chair conformation, with the methyl substituents equatorial. All H



**Figure 1**

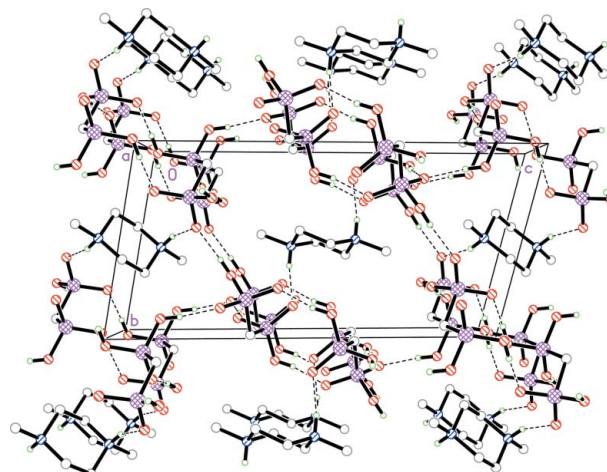
The two cations (completed by inversion symmetry) and two anions in the asymmetric unit of (I), showing atom labels and with 50% probability displacement ellipsoids. [Symmetry codes: (i)  $1 - x, 1 - y, -z$ ; (ii)  $1 - x, 1 - y, 1 - z$ .]

atoms bonded to N in the cations and to O in the anions were clearly identified in a difference map. The P—O bond lengths to the OH groups are all longer than those to unprotonated O atoms (Table 1). The shortest P—O bonds (P2—O6 and P4—O12) are found in the intact P(O)(OH)<sub>2</sub> phosphonic acid groups of the anions and can be assigned as P=O double bonds. The P—O bonds to unprotonated O atoms in the deprotonated P(O)<sub>2</sub>(OH) phosphonate groups are intermediate in length; these are delocalized and intermediate between single and double bonds and can be assumed to carry the delocalised negative charge, while the P—OH bonds are single. Methylidiphosphonates in crystal structures are usually dianionic, with both groups deprotonated. Only in one previous report is a singly charged H<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>H<sup>−</sup> anion found (Hmimid *et al.*, 1987); in this trihallium(I) compound, singly and doubly charged anions occupy the same position and are, therefore, disordered.

All N—H and O—H groups act as hydrogen-bond donors in the crystal structure of (I) (Fig. 2, Table 2). The acceptors are the unprotonated O atoms of the anions; since there are only six of these for the eight donors, two (atoms O2 and O8, which carry some shared negative charge in the delocalized phosphonate groups) are double acceptors. The hydrogen bonding generates a three-dimensional network.

## Experimental

The title compound was obtained by hydrothermal synthesis, in an attempt to prepare an aluminium methylenediphosphonate complex. A mixture of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O (98%, Alfa Aesar), methylenediphosphonic acid (98%, Alfa Aesar), hydrofluoric acid (48 wt.% in water, Aldrich), trimethylamine (48% in water, Fluka) and ethanol was combined in the molar ratio 1.3:9.43:9.52:100. Vigorous stirring led to complete dissolution of all reagents. The solution was then placed in a 23 ml Teflon-lined stainless steel autoclave and heated at 473 K for 10 d. The title compound, (I), was collected by filtration, washed with deionized water and air-dried. It is not known whether aluminium-containing products were in the resulting solid or in the filtrate. The solid material was largely an unidentified powder mixture containing single crystals of the title compound.



**Figure 2**

The packing of the ions, viewed down the *a* axis, with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

## Crystal data

C<sub>6</sub>H<sub>16</sub>N<sub>2</sub><sup>2+</sup>·2CH<sub>5</sub>O<sub>6</sub>P<sub>2</sub><sup>−</sup>  
*M<sub>r</sub>* = 466.19  
 Triclinic, *P* $\bar{1}$   
*a* = 6.9881 (6) Å  
*b* = 8.9148 (6) Å  
*c* = 16.6251 (10) Å  
 $\alpha$  = 98.910 (5)°  
 $\beta$  = 95.882 (6)°  
 $\gamma$  = 112.244 (6)°  
*V* = 932.24 (12) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.661 Mg m<sup>−3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 59 reflections  
 $\theta$  = 2.5–27.5°  
 $\mu$  = 0.47 mm<sup>−1</sup>  
*T* = 120 (2) K  
 Block, colourless  
 0.50 × 0.50 × 0.20 mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
*T<sub>min</sub>* = 0.800, *T<sub>max</sub>* = 0.915  
 12295 measured reflections

4037 independent reflections  
 3592 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.028  
 $\theta_{max}$  = 27.5°  
*h* = −9 → 9  
*k* = −11 → 11  
*l* = −21 → 21

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.028  
*wR* (*F*<sup>2</sup>) = 0.075  
*S* = 1.06  
 4037 reflections  
 262 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.7406P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.55 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.50 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXTL (Sheldrick, 2001)  
 Extinction coefficient: 0.011 (2)

**Table 1**

Selected bond lengths (Å).

P1—C1	1.8118 (16)	P3—C2	1.8088 (16)
P1—O1	1.5666 (12)	P3—O7	1.5646 (13)
P1—O2	1.5119 (11)	P3—O8	1.5312 (12)
P1—O3	1.5180 (11)	P3—O9	1.5055 (12)
P2—C1	1.8000 (16)	P4—C2	1.8021 (16)
P2—O4	1.5703 (12)	P4—O10	1.5494 (12)
P2—O5	1.5401 (11)	P4—O11	1.5583 (12)
P2—O6	1.4939 (12)	P4—O12	1.5005 (12)

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

<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>
O1—H1O···O6 <sup>iii</sup>	0.81 (2)	1.73 (2)	2.5287 (16)	169 (2)
O4—H4O···O8 <sup>iv</sup>	0.83 (2)	1.76 (2)	2.5799 (17)	174 (2)
O5—H5O···O3 <sup>v</sup>	0.84 (2)	1.63 (2)	2.4689 (16)	177 (2)
O7—H7O···O2	0.83 (2)	1.71 (2)	2.5139 (16)	162 (2)
O10—H10O···O8 <sup>vi</sup>	0.82 (2)	1.73 (2)	2.5228 (17)	163 (2)
O11—H11O···O9 <sup>vii</sup>	0.83 (2)	1.70 (2)	2.5222 (17)	169 (2)
N1—H1N···O2	0.86 (2)	1.97 (2)	2.7802 (18)	157 (2)
N2—H2N···O12	0.88 (2)	1.79 (2)	2.6563 (18)	170 (2)

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

C-bound H atoms were positioned geometrically and refined with a riding model (including free rotation about C—C bonds), with C—H = 0.98 (CH<sub>2</sub>) or 0.99 Å (CH<sub>3</sub>) and with  $U_{\text{iso}}(\text{H}) = 1.2$  (1.5 for methyl groups) times  $U_{\text{eq}}(\text{C})$ . H atoms bonded to N and O were located in a difference map and refined with restrained distances of N—H = 0.87 (2) Å and O—H = 0.84 (2) Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXTL*

(Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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## supporting information

*Acta Cryst.* (2005). E61, o2635–o2637 [https://doi.org/10.1107/S1600536805022737]

## *N,N'*-Dimethylpiperazinium(2+) bis[methylenehydrogendiphosphonate(1-)]

Zhanhui Yuan and William Clegg

### *N,N'*-Dimethylpiperazinium(2+) bis[methylenehydrogendiphosphonate(1-)]

#### Crystal data

$C_6H_{16}N_2^{2+} \cdot 2CH_5O_6P_2^-$   
 $M_r = 466.19$   
 Triclinic,  $P\bar{1}$   
 Hall symbol:  $-P\ 1$   
 $a = 6.9881$  (6) Å  
 $b = 8.9148$  (6) Å  
 $c = 16.6251$  (10) Å  
 $\alpha = 98.910$  (5)°  
 $\beta = 95.882$  (6)°  
 $\gamma = 112.244$  (6)°  
 $V = 932.24$  (12) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 488$   
 $D_x = 1.661$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 59 reflections  
 $\theta = 2.5$ – $27.5$ °  
 $\mu = 0.47$  mm<sup>-1</sup>  
 $T = 120$  K  
 Block, colourless  
 $0.50 \times 0.50 \times 0.20$  mm

#### Data collection

Nonius KappaCCD area-detector  
 diffractometer  
 Radiation source: sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2002)  
 $T_{\min} = 0.800$ ,  $T_{\max} = 0.915$

12295 measured reflections  
 4037 independent reflections  
 3592 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\max} = 27.5$ °,  $\theta_{\min} = 4.7$ °  
 $h = -9 \rightarrow 9$   
 $k = -11 \rightarrow 11$   
 $l = -21 \rightarrow 21$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.075$   
 $S = 1.06$   
 4037 reflections  
 262 parameters  
 8 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: difference Fourier map  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.7406P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.55$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.50$  e Å<sup>-3</sup>  
 Extinction correction: SHELXTL (Sheldrick,  
 2001),  $F_c^* = kFc[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.011 (2)

#### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.72874 (6)	0.26531 (5)	0.14321 (2)	0.01031 (10)

P2	0.25336 (6)	0.05401 (5)	0.11556 (2)	0.01102 (10)
C1	0.5149 (2)	0.08775 (19)	0.16149 (10)	0.0132 (3)
H1A	0.5392	-0.0127	0.1409	0.016*
H1B	0.5212	0.0993	0.2220	0.016*
O1	0.92324 (18)	0.27350 (16)	0.20257 (7)	0.0175 (3)
H1O	1.003 (3)	0.242 (3)	0.1799 (13)	0.021*
O2	0.68992 (18)	0.41979 (14)	0.16996 (7)	0.0157 (2)
O3	0.75543 (18)	0.23748 (14)	0.05337 (7)	0.0155 (2)
O4	0.10390 (18)	-0.11161 (15)	0.13683 (7)	0.0175 (2)
H4O	0.134 (3)	-0.123 (3)	0.1844 (10)	0.021*
O5	0.23587 (19)	0.02151 (14)	0.02082 (7)	0.0152 (2)
H5O	0.241 (3)	-0.067 (2)	-0.0027 (12)	0.018*
O6	0.20780 (18)	0.20123 (15)	0.14673 (7)	0.0187 (3)
P3	1.01122 (6)	0.79458 (5)	0.33650 (2)	0.01223 (11)
P4	0.72510 (6)	0.96071 (5)	0.39958 (2)	0.01142 (11)
C2	0.9692 (2)	0.98231 (19)	0.36560 (10)	0.0131 (3)
H2A	1.0856	1.0583	0.4105	0.016*
H2B	0.9788	1.0364	0.3176	0.016*
O7	0.79361 (19)	0.67144 (16)	0.28394 (8)	0.0228 (3)
H7O	0.785 (4)	0.590 (2)	0.2495 (12)	0.027*
O8	1.17930 (18)	0.83067 (16)	0.28150 (7)	0.0191 (3)
O9	1.0655 (2)	0.73429 (14)	0.41184 (7)	0.0186 (3)
O10	0.56949 (19)	0.90998 (16)	0.31701 (7)	0.0191 (3)
H10O	0.444 (3)	0.888 (3)	0.3155 (13)	0.023*
O11	0.7503 (2)	1.13825 (15)	0.44042 (7)	0.0194 (3)
H11O	0.801 (3)	1.169 (3)	0.4905 (10)	0.023*
O12	0.66895 (18)	0.84128 (14)	0.45641 (7)	0.0151 (2)
N1	0.4264 (2)	0.52382 (16)	0.07827 (8)	0.0121 (3)
H1N	0.476 (3)	0.467 (2)	0.1047 (11)	0.014*
C3	0.6069 (2)	0.65879 (19)	0.05574 (10)	0.0139 (3)
H3A	0.7063	0.7294	0.1067	0.017*
H3B	0.5533	0.7294	0.0281	0.017*
C4	0.2785 (2)	0.41262 (19)	0.00124 (10)	0.0140 (3)
H4A	0.2157	0.4764	-0.0278	0.017*
H4B	0.1635	0.3212	0.0162	0.017*
C5	0.3156 (3)	0.5972 (2)	0.13405 (10)	0.0181 (3)
H5A	0.2560	0.6615	0.1050	0.027*
H5B	0.4155	0.6700	0.1836	0.027*
H5C	0.2026	0.5082	0.1502	0.027*
N2	0.4365 (2)	0.51721 (17)	0.41761 (8)	0.0143 (3)
H2N	0.513 (3)	0.6236 (19)	0.4239 (12)	0.017*
C6	0.5842 (3)	0.4356 (2)	0.43334 (10)	0.0167 (3)
H6A	0.6815	0.4544	0.3931	0.020*
H6B	0.5037	0.3146	0.4259	0.020*
C7	0.2916 (3)	0.4945 (2)	0.47959 (10)	0.0161 (3)
H7A	0.2037	0.3750	0.4734	0.019*
H7B	0.1972	0.5515	0.4692	0.019*
C8	0.3153 (3)	0.4548 (2)	0.33170 (11)	0.0248 (4)

H8A	0.2222	0.3375	0.3244	0.037*
H8B	0.4127	0.4669	0.2923	0.037*
H8C	0.2313	0.5188	0.3218	0.037*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
P1	0.0091 (2)	0.01140 (19)	0.00927 (18)	0.00425 (15)	-0.00039 (14)	-0.00018 (14)
P2	0.0095 (2)	0.0112 (2)	0.01111 (19)	0.00410 (15)	-0.00016 (14)	0.00013 (14)
C1	0.0130 (8)	0.0132 (7)	0.0141 (7)	0.0060 (6)	0.0006 (6)	0.0040 (6)
O1	0.0107 (6)	0.0273 (6)	0.0142 (5)	0.0097 (5)	-0.0008 (4)	0.0005 (5)
O2	0.0152 (6)	0.0122 (5)	0.0168 (6)	0.0057 (4)	-0.0021 (4)	-0.0022 (4)
O3	0.0182 (6)	0.0181 (6)	0.0109 (5)	0.0083 (5)	0.0028 (4)	0.0024 (4)
O4	0.0143 (6)	0.0189 (6)	0.0139 (6)	0.0011 (5)	-0.0006 (5)	0.0049 (5)
O5	0.0198 (6)	0.0138 (6)	0.0106 (5)	0.0064 (5)	-0.0002 (4)	0.0013 (4)
O6	0.0139 (6)	0.0188 (6)	0.0229 (6)	0.0095 (5)	0.0006 (5)	-0.0030 (5)
P3	0.0101 (2)	0.0138 (2)	0.01052 (19)	0.00387 (16)	0.00048 (14)	-0.00079 (14)
P4	0.0123 (2)	0.0119 (2)	0.00977 (18)	0.00505 (15)	0.00051 (14)	0.00160 (14)
C2	0.0117 (8)	0.0113 (7)	0.0137 (7)	0.0027 (6)	0.0001 (6)	0.0020 (6)
O7	0.0124 (6)	0.0216 (6)	0.0251 (7)	0.0046 (5)	-0.0014 (5)	-0.0130 (5)
O8	0.0127 (6)	0.0325 (7)	0.0137 (5)	0.0107 (5)	0.0024 (4)	0.0051 (5)
O9	0.0268 (7)	0.0155 (6)	0.0160 (6)	0.0111 (5)	0.0032 (5)	0.0037 (4)
O10	0.0120 (6)	0.0320 (7)	0.0128 (5)	0.0093 (5)	-0.0004 (5)	0.0039 (5)
O11	0.0300 (7)	0.0160 (6)	0.0157 (6)	0.0136 (5)	0.0035 (5)	0.0027 (5)
O12	0.0176 (6)	0.0129 (5)	0.0131 (5)	0.0045 (5)	0.0026 (4)	0.0025 (4)
N1	0.0129 (7)	0.0118 (6)	0.0112 (6)	0.0049 (5)	0.0010 (5)	0.0025 (5)
C3	0.0130 (8)	0.0104 (7)	0.0147 (7)	0.0017 (6)	0.0012 (6)	0.0013 (6)
C4	0.0111 (8)	0.0144 (7)	0.0132 (7)	0.0026 (6)	-0.0002 (6)	0.0015 (6)
C5	0.0215 (9)	0.0168 (8)	0.0187 (8)	0.0094 (7)	0.0082 (7)	0.0032 (6)
N2	0.0150 (7)	0.0110 (6)	0.0133 (6)	0.0021 (5)	-0.0024 (5)	0.0035 (5)
C6	0.0198 (9)	0.0159 (8)	0.0157 (8)	0.0086 (7)	0.0026 (6)	0.0029 (6)
C7	0.0129 (8)	0.0148 (8)	0.0197 (8)	0.0047 (6)	0.0001 (6)	0.0049 (6)
C8	0.0276 (10)	0.0234 (9)	0.0135 (8)	0.0025 (7)	-0.0075 (7)	0.0028 (7)

*Geometric parameters (Å, °)*

P1—C1	1.8118 (16)	N1—H1N	0.857 (15)
P1—O1	1.5666 (12)	N1—C3	1.505 (2)
P1—O2	1.5119 (11)	N1—C4	1.5002 (19)
P1—O3	1.5180 (11)	N1—C5	1.493 (2)
P2—C1	1.8000 (16)	C3—H3A	0.990
P2—O4	1.5703 (12)	C3—H3B	0.990
P2—O5	1.5401 (11)	C3—C4 <sup>i</sup>	1.516 (2)
P2—O6	1.4939 (12)	C4—C3 <sup>i</sup>	1.516 (2)
C1—H1A	0.990	C4—H4A	0.990
C1—H1B	0.990	C4—H4B	0.990
O1—H1O	0.813 (15)	C5—H5A	0.980
O4—H4O	0.827 (15)	C5—H5B	0.980

O5—H5O	0.837 (15)	C5—H5C	0.980
P3—C2	1.8088 (16)	N2—H2N	0.877 (15)
P3—O7	1.5646 (13)	N2—C6	1.495 (2)
P3—O8	1.5312 (12)	N2—C7	1.501 (2)
P3—O9	1.5055 (12)	N2—C8	1.489 (2)
P4—C2	1.8021 (16)	C6—H6A	0.990
P4—O10	1.5494 (12)	C6—H6B	0.990
P4—O11	1.5583 (12)	C6—C7 <sup>ii</sup>	1.514 (2)
P4—O12	1.5005 (12)	C7—C6 <sup>ii</sup>	1.514 (2)
C2—H2A	0.990	C7—H7A	0.990
C2—H2B	0.990	C7—H7B	0.990
O7—H7O	0.832 (16)	C8—H8A	0.980
O10—H10O	0.818 (16)	C8—H8B	0.980
O11—H11O	0.829 (16)	C8—H8C	0.980
C1—P1—O1	103.11 (7)	C3—N1—C4	109.82 (12)
C1—P1—O2	109.22 (7)	C3—N1—C5	110.34 (12)
C1—P1—O3	110.38 (7)	C4—N1—C5	110.96 (13)
O1—P1—O2	109.23 (7)	N1—C3—H3A	109.4
O1—P1—O3	111.51 (7)	N1—C3—H3B	109.4
O2—P1—O3	112.92 (7)	N1—C3—C4 <sup>i</sup>	111.34 (12)
C1—P2—O4	105.78 (7)	H3A—C3—H3B	108.0
C1—P2—O5	108.65 (7)	H3A—C3—C4 <sup>i</sup>	109.4
C1—P2—O6	109.88 (7)	H3B—C3—C4 <sup>i</sup>	109.4
O4—P2—O5	106.64 (6)	N1—C4—C3 <sup>i</sup>	110.63 (13)
O4—P2—O6	114.36 (7)	N1—C4—H4A	109.5
O5—P2—O6	111.23 (7)	N1—C4—H4B	109.5
P1—C1—P2	116.93 (9)	C3 <sup>i</sup> —C4—H4A	109.5
P1—C1—H1A	108.1	C3 <sup>i</sup> —C4—H4B	109.5
P1—C1—H1B	108.1	H4A—C4—H4B	108.1
P2—C1—H1A	108.1	N1—C5—H5A	109.5
P2—C1—H1B	108.1	N1—C5—H5B	109.5
H1A—C1—H1B	107.3	N1—C5—H5C	109.5
P1—O1—H1O	115.0 (15)	H5A—C5—H5B	109.5
P2—O4—H4O	115.0 (15)	H5A—C5—H5C	109.5
P2—O5—H5O	117.6 (14)	H5B—C5—H5C	109.5
C2—P3—O7	102.53 (7)	H2N—N2—C6	107.1 (13)
C2—P3—O8	107.44 (7)	H2N—N2—C7	108.3 (13)
C2—P3—O9	110.87 (7)	H2N—N2—C8	108.2 (13)
O7—P3—O8	109.91 (7)	C6—N2—C7	110.51 (12)
O7—P3—O9	111.51 (8)	C6—N2—C8	111.70 (14)
O8—P3—O9	113.90 (7)	C7—N2—C8	110.83 (13)
C2—P4—O10	102.76 (7)	N2—C6—H6A	109.6
C2—P4—O11	106.61 (7)	N2—C6—H6B	109.6
C2—P4—O12	111.73 (7)	N2—C6—C7 <sup>ii</sup>	110.13 (13)
O10—P4—O11	106.19 (7)	H6A—C6—H6B	108.1
O10—P4—O12	115.59 (7)	H6A—C6—C7 <sup>ii</sup>	109.6
O11—P4—O12	113.07 (7)	H6B—C6—C7 <sup>ii</sup>	109.6

P3—C2—P4	117.02 (9)	N2—C7—C6 <sup>ii</sup>	110.51 (13)
P3—C2—H2A	108.0	N2—C7—H7A	109.5
P3—C2—H2B	108.0	N2—C7—H7B	109.5
P4—C2—H2A	108.0	C6 <sup>ii</sup> —C7—H7A	109.5
P4—C2—H2B	108.0	C6 <sup>ii</sup> —C7—H7B	109.5
H2A—C2—H2B	107.3	H7A—C7—H7B	108.1
P3—O7—H7O	120.5 (16)	N2—C8—H8A	109.5
P4—O10—H10O	122.2 (15)	N2—C8—H8B	109.5
P4—O11—H11O	115.4 (15)	N2—C8—H8C	109.5
H1N—N1—C3	108.3 (13)	H8A—C8—H8B	109.5
H1N—N1—C4	109.5 (13)	H8A—C8—H8C	109.5
H1N—N1—C5	107.9 (13)	H8B—C8—H8C	109.5
O4—P2—C1—P1	176.67 (8)	O8—P3—C2—P4	159.45 (8)
O5—P2—C1—P1	62.49 (10)	O9—P3—C2—P4	-75.49 (10)
O6—P2—C1—P1	-59.41 (11)	C4—N1—C3—C4 <sup>i</sup>	-57.12 (18)
O1—P1—C1—P2	171.03 (8)	C5—N1—C3—C4 <sup>i</sup>	-179.74 (13)
O2—P1—C1—P2	54.97 (11)	C3—N1—C4—C3 <sup>i</sup>	56.70 (18)
O3—P1—C1—P2	-69.75 (10)	C5—N1—C4—C3 <sup>i</sup>	178.95 (13)
O10—P4—C2—P3	-81.93 (10)	C7—N2—C6—C7 <sup>ii</sup>	-57.62 (18)
O11—P4—C2—P3	166.60 (8)	C8—N2—C6—C7 <sup>ii</sup>	178.50 (14)
O12—P4—C2—P3	42.61 (11)	C6—N2—C7—C6 <sup>ii</sup>	57.84 (18)
O7—P3—C2—P4	43.63 (11)	C8—N2—C7—C6 <sup>ii</sup>	-177.78 (14)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O $\cdots$ O6 <sup>iii</sup>	0.81 (2)	1.73 (2)	2.5287 (16)	169 (2)
O4—H4O $\cdots$ O8 <sup>iv</sup>	0.83 (2)	1.76 (2)	2.5799 (17)	174 (2)
O5—H5O $\cdots$ O3 <sup>v</sup>	0.84 (2)	1.63 (2)	2.4689 (16)	177 (2)
O7—H7O $\cdots$ O2	0.83 (2)	1.71 (2)	2.5139 (16)	162 (2)
O10—H10O $\cdots$ O8 <sup>vi</sup>	0.82 (2)	1.73 (2)	2.5228 (17)	163 (2)
O11—H11O $\cdots$ O9 <sup>vii</sup>	0.83 (2)	1.70 (2)	2.5222 (17)	169 (2)
N1—H1N $\cdots$ O2	0.86 (2)	1.97 (2)	2.7802 (18)	157 (2)
N2—H2N $\cdots$ O12	0.88 (2)	1.79 (2)	2.6563 (18)	170 (2)

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