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3-Chloro-2-methylanilinium dihydrogenphosphate

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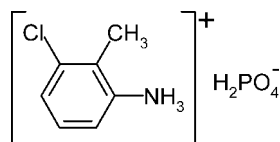
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Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
 R factor = 0.044; wR factor = 0.122; data-to-parameter ratio = 14.6.

The structure of the title compound, $\text{C}_7\text{H}_9\text{ClN}^+\cdot\text{H}_2\text{PO}_4^-$, contains inorganic layers built by $(\text{H}_2\text{PO}_4)^-$ anions and which are parallel to the ab planes around $z = \frac{1}{2}$. 3-Chloro-2-methylanilinium cations are anchored between the inorganic layers through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. Electrostatic and van der Waals interactions, as well as hydrogen bonds, maintain the structural cohesion.

Related literature

For related literature, see: Adams (1977); Blessing (1986); Chtioui & Jouini (2004); Desiraju (1989, 1995); Hebert (1978); Oueslati & Ben Nasr (2006).



Experimental

Crystal data

$\text{C}_7\text{H}_9\text{ClN}^+\cdot\text{H}_2\text{PO}_4^-$
 $M_r = 239.59$
 Monoclinic, $P2_1/c$
 $a = 16.942$ (6) Å
 $b = 8.272$ (2) Å
 $c = 7.979$ (7) Å
 $\beta = 100.11$ (5)°

$V = 1100.8$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.48$ mm⁻¹
 $T = 292$ K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

Enraf-Nonius TurboCAD-4
 diffractometer
 Absorption correction: none
 3304 measured reflections
 1932 independent reflections

1736 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 2 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.122$
 $S = 1.08$
 1932 reflections

132 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O3}^{\text{ii}}$	0.82	1.83	2.634 (3)	166
$\text{O2}-\text{H2}\cdots\text{O3}^{\text{ii}}$	0.82	1.83	2.596 (2)	154
$\text{N1}-\text{H1A}\cdots\text{O3}$	0.89	2.04	2.886 (3)	158
$\text{N1}-\text{H1B}\cdots\text{O4}^{\text{iii}}$	0.89	1.84	2.722 (3)	172
$\text{N1}-\text{H1C}\cdots\text{O4}^{\text{ii}}$	0.89	1.84	2.708 (3)	166

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

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2313).

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S1. Comment

Inorganic-organic hybrid materials have been studied extensively because the blending of organic and inorganic components allows to the development of materials with novel properties. In particular the family of material which combine monophosphate anions with organic molecules such as aliphatic and aromatic amines has been studied intensively due to their numerous uses in various fields such as biomolecular science, liquid crystals, catalysts and fuel cells (Adams, 1977; Blessing, 1986; Desiraju, 1989, 1995). As a contribution to the study of this compound family, we report in this work the synthesis and the crystal structure of a new organic cation monophosphate [3-Cl-2-CH₃C₆H₃NH₃]⁺H₂PO₄⁻ (I).

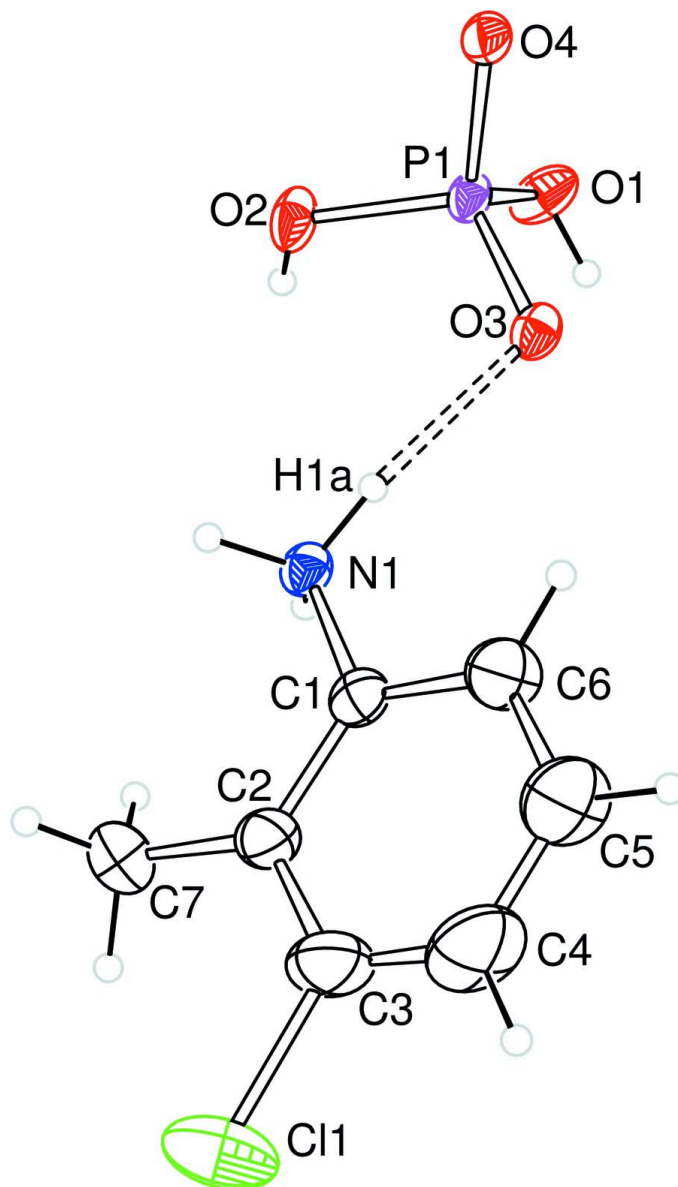
The asymmetric unit in the structure of I consists of one phosphate anion (H₂PO₄)⁻ and one organic cation (3-Cl-2-CH₃C₆H₃NH₃)⁺ (Fig. 1). A projection of the structure in the [001] direction shows that the (H₂PO₄) groups are interconnected by O—H...O hydrogen bonds to form inorganic layers parallel to the (a, b) planes (Fig. 2). On both sides of each inorganic layer (Fig. 3), are grafted the organic cations compensating their negatives charges. Each (H₂PO₄) group is connected to three neighbours by strong hydrogen bonds, with O...O separations ranging from 2.596 (2) Å to 2.634 (3) Å (Table 1). Among the P—O distances in the PO₄ tetrahedron, we can distinguish two different types: the shortest ones (1.498 (2) Å and 1.509 (2) Å) correspond to the phosphorus atom double bonded to oxygen atom (P=O); the largest ones (1.563 (2) Å and 1.564 (2) Å) can be attributed to P—OH distances. The average P—O distances and O—P—O bond angles are 1.534 Å and 109.42°, respectively, which fall in the range of the values observed in many phosphate materials (Hebert, 1978)). The strength of O—H...O hydrogen bond and the values of P...P distances (with a minimum value of 4.383 (4) Å) between two successive inorganic layers could allow us to consider the (H₂PO₄)_n⁻ subnetwork as a polymeric species. Similar arrangement have been observed in other crystal structures (Chtioui & Jouini, 2004). The C—C bond lengths spreading between are 1.361 (6) and 1.500 (5) Å, which are between single and double bond and agree with that in 4-chloroanilinium dihydrogenmonophosphate (Oueslati & Ben Nasr, 2006).

S2. Experimental

Single crystals of the title compound (I) were prepared by adding drop by drop under stirring, an aqueous solution (10 ml) of orthophosphoric acid (0.25 mmol) (85 weight from Fluka %) to an alcoholic solution (10 ml) of 3-Chloro-2-methylaniline (0.15 mmol)(Across 98). The obtained solution was then slowly evaporated at room temperature until the formation of single crystals which were stable under normal condition of temperature and humidity.

S3. Refinement

All H atoms attached to C, N and O atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (C_{aromatic}) or 0.96 Å (C_{methyl}), N—H = 0.89 Å and O—H = 0.82 Å and with $U_{\text{iso}}=1.2U_{\text{eq}}(\text{C}_{\text{aromatic}},\text{O})$ or $U_{\text{iso}}=1.5U_{\text{eq}}(\text{C}_{\text{methyl}},\text{N})$.

**Figure 1**

View of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. H bond is shown as dashed line.

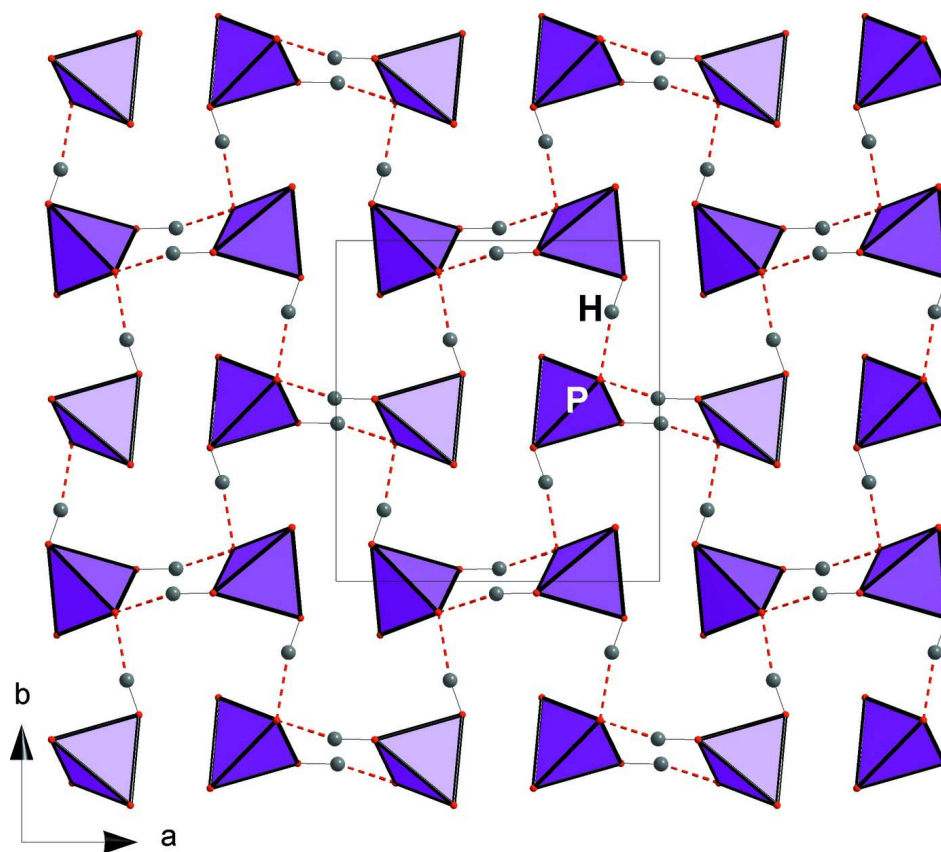


Figure 2

Projection of $(\text{H}_2\text{PO}_4)_n^-$ subnetwork along c axis.

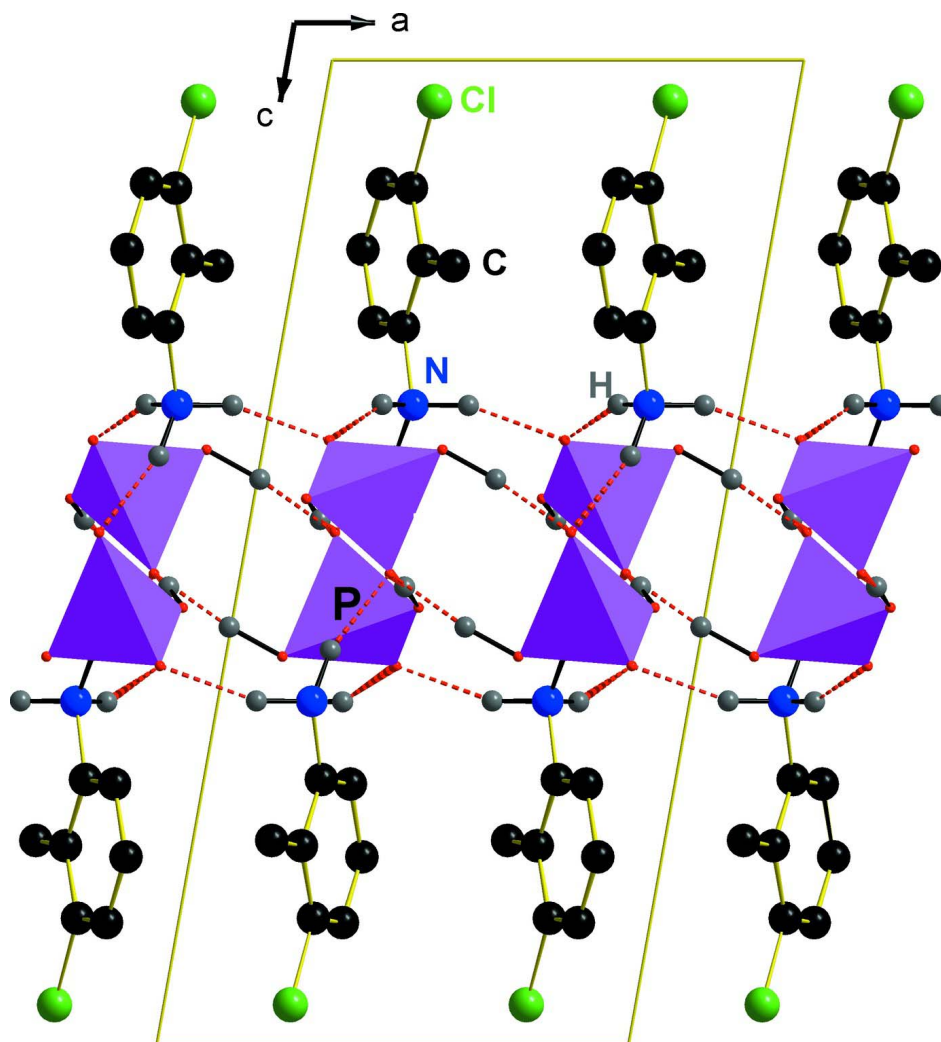


Figure 3
Projection of (I) along *b* axis.

3-Chloro-2-methylanilinium dihydrogenphosphate

Crystal data

$C_7H_9ClN^+ \cdot H_2PO_4^-$
 $M_r = 239.59$
 Monoclinic, $P2_1/c$
 Hall symbol: $-P 2_1/c$
 $a = 16.942(6) \text{ \AA}$
 $b = 8.272(2) \text{ \AA}$
 $c = 7.979(7) \text{ \AA}$
 $\beta = 100.11(5)^\circ$
 $V = 1100.8(11) \text{ \AA}^3$
 $Z = 4$

$F(000) = 496$
 $D_x = 1.446 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 8\text{--}11^\circ$
 $\mu = 0.48 \text{ mm}^{-1}$
 $T = 292 \text{ K}$
 Prism, colorless
 $0.40 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Enraf–Nonius TurboCAD4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

non-profiled ω scans

3304 measured reflections

1932 independent reflections

1736 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.027$$

$$\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 2.4^\circ$$

$$h = -10 \rightarrow 20$$

$$k = -9 \rightarrow 0$$

$$l = -9 \rightarrow 9$$

2 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.044$$

$$wR(F^2) = 0.122$$

$$S = 1.08$$

1932 reflections

132 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.6257P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.011$$

$$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.015 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.43820 (3)	0.46630 (6)	0.23711 (6)	0.0298 (2)
O1	0.39492 (10)	0.5342 (2)	0.3800 (2)	0.0503 (5)
H1	0.4278	0.5477	0.4674	0.075*
O2	0.44438 (12)	0.60754 (19)	0.11002 (19)	0.0462 (5)
H2	0.4562	0.6914	0.1634	0.069*
O3	0.52069 (9)	0.40766 (18)	0.31601 (17)	0.0346 (4)
O4	0.38537 (10)	0.34256 (19)	0.13619 (18)	0.0408 (4)
C11	0.95781 (6)	0.6138 (3)	0.2672 (2)	0.1564 (8)
N1	0.65051 (11)	0.5738 (2)	0.1985 (2)	0.0342 (4)
H1A	0.6130	0.5026	0.2138	0.051*
H1B	0.6435	0.6023	0.0893	0.051*
H1C	0.6468	0.6609	0.2621	0.051*
C1	0.72967 (14)	0.5010 (3)	0.2480 (3)	0.0392 (5)
C2	0.79647 (15)	0.5918 (4)	0.2317 (3)	0.0524 (7)
C3	0.86992 (18)	0.5110 (6)	0.2839 (5)	0.0784 (10)

C4	0.8752 (2)	0.3579 (6)	0.3475 (6)	0.0954 (13)
H4	0.9252	0.3102	0.3805	0.114*
C5	0.8074 (2)	0.2742 (5)	0.3631 (6)	0.0875 (12)
H5	0.8110	0.1701	0.4078	0.105*
C6	0.73348 (18)	0.3460 (3)	0.3116 (4)	0.0617 (8)
H6	0.6867	0.2900	0.3199	0.074*
C7	0.7899 (2)	0.7623 (5)	0.1667 (5)	0.0807 (11)
H7A	0.7432	0.8123	0.1966	0.121*
H7B	0.7856	0.7619	0.0451	0.121*
H7C	0.8368	0.8219	0.2168	0.121*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0413 (4)	0.0243 (3)	0.0221 (3)	−0.0007 (2)	0.0007 (2)	−0.00082 (18)
O1	0.0444 (9)	0.0731 (13)	0.0312 (9)	0.0113 (9)	0.0005 (7)	−0.0125 (8)
O2	0.0800 (12)	0.0248 (8)	0.0297 (8)	−0.0045 (8)	−0.0020 (8)	0.0030 (6)
O3	0.0448 (9)	0.0301 (8)	0.0276 (7)	0.0037 (6)	0.0023 (6)	−0.0020 (6)
O4	0.0548 (9)	0.0355 (9)	0.0285 (7)	−0.0119 (7)	−0.0026 (7)	0.0004 (6)
Cl1	0.0485 (6)	0.2330 (19)	0.1867 (15)	−0.0312 (8)	0.0178 (7)	0.0464 (14)
N1	0.0391 (10)	0.0352 (9)	0.0272 (8)	−0.0005 (8)	0.0029 (7)	−0.0024 (7)
C1	0.0416 (12)	0.0449 (12)	0.0305 (11)	0.0019 (10)	0.0048 (9)	−0.0055 (9)
C2	0.0451 (14)	0.0698 (18)	0.0419 (13)	−0.0073 (13)	0.0061 (11)	−0.0006 (13)
C3	0.0414 (15)	0.118 (3)	0.075 (2)	−0.0034 (18)	0.0094 (15)	0.001 (2)
C4	0.060 (2)	0.113 (3)	0.109 (3)	0.035 (2)	0.005 (2)	0.011 (3)
C5	0.072 (2)	0.066 (2)	0.120 (3)	0.0236 (18)	0.005 (2)	0.017 (2)
C6	0.0540 (15)	0.0458 (15)	0.083 (2)	0.0069 (13)	0.0066 (14)	0.0043 (14)
C7	0.075 (2)	0.085 (2)	0.079 (2)	−0.0277 (19)	0.0063 (18)	0.0238 (19)

Geometric parameters (Å, °)

P1—O4	1.4980 (16)	C1—C2	1.383 (4)
P1—O3	1.5087 (17)	C2—C3	1.409 (4)
P1—O2	1.5626 (17)	C2—C7	1.500 (5)
P1—O1	1.5641 (19)	C3—C4	1.361 (6)
O1—H1	0.8200	C4—C5	1.365 (6)
O2—H2	0.8200	C4—H4	0.9300
Cl1—C3	1.740 (4)	C5—C6	1.382 (4)
N1—C1	1.460 (3)	C5—H5	0.9300
N1—H1A	0.8900	C6—H6	0.9300
N1—H1B	0.8900	C7—H7A	0.9600
N1—H1C	0.8900	C7—H7B	0.9600
C1—C6	1.377 (4)	C7—H7C	0.9600
O4—P1—O3	115.27 (9)	C3—C2—C7	123.8 (3)
O4—P1—O2	105.31 (10)	C4—C3—C2	123.3 (3)
O3—P1—O2	110.39 (10)	C4—C3—Cl1	118.8 (3)
O4—P1—O1	108.96 (11)	C2—C3—Cl1	117.9 (3)

O3—P1—O1	109.25 (10)	C3—C4—C5	120.3 (3)
O2—P1—O1	107.34 (11)	C3—C4—H4	119.9
P1—O1—H1	109.5	C5—C4—H4	119.9
P1—O2—H2	109.5	C4—C5—C6	119.2 (4)
C1—N1—H1A	109.5	C4—C5—H5	120.4
C1—N1—H1B	109.5	C6—C5—H5	120.4
H1A—N1—H1B	109.5	C1—C6—C5	119.4 (3)
C1—N1—H1C	109.5	C1—C6—H6	120.3
H1A—N1—H1C	109.5	C5—C6—H6	120.3
H1B—N1—H1C	109.5	C2—C7—H7A	109.5
C6—C1—C2	123.7 (3)	C2—C7—H7B	109.5
C6—C1—N1	117.7 (2)	H7A—C7—H7B	109.5
C2—C1—N1	118.6 (2)	C2—C7—H7C	109.5
C1—C2—C3	114.2 (3)	H7A—C7—H7C	109.5
C1—C2—C7	122.1 (3)	H7B—C7—H7C	109.5

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...O3 ⁱ	0.82	1.83	2.634 (3)	166
O2—H2...O3 ⁱⁱ	0.82	1.83	2.596 (2)	154
N1—H1A...O3	0.89	2.04	2.886 (3)	158
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