

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# 4,7-Phenanthroline perchlorate–5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one–water (1/1/2)

Ana B. Caballero, Miguel Quirós\* and Juan M. Salas

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Correspondence e-mail: mquirós@ugr.es

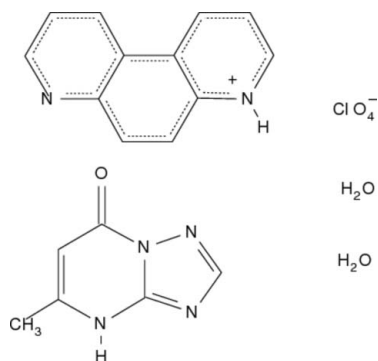
Received 15 January 2010; accepted 20 January 2010

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}–\text{C}) = 0.003$  Å;  $R$  factor = 0.054;  $wR$  factor = 0.152; data-to-parameter ratio = 15.4.

The asymmetric unit of the title compound,  $\text{C}_{12}\text{H}_9\text{N}_2^+ \cdot \text{ClO}_4^- \cdot \text{C}_6\text{H}_6\text{N}_4\text{O} \cdot 2\text{H}_2\text{O}$ , contains a monoprotonated 4,7-phenanthroline (47phen) cation, a perchlorate anion balancing its charge, a neutral molecule of 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (HmtpO) and two interstitial water molecules. In the crystal structure, the acidic H atoms of 47phenH<sup>+</sup> and HmtpO form strong hydrogen bonds with the water molecules, which in turn act as hydrogen-bond donors, forming links between them and towards the carbonyl O atom of HmtpO, the non-protonated N atom of 47phen<sup>+</sup> and one of the O atoms of the anion.

## Related literature

For other structures containing perchlorate and protonated 4,7-phenanthroline, see: Shang *et al.* (2006); Gillard *et al.* (1998). For other structures containing neutral and non-coordinated 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one, see: Navarro *et al.* (1997); Salas *et al.* (1996).



## Experimental

## Crystal data

$\text{C}_{12}\text{H}_9\text{N}_2^+ \cdot \text{ClO}_4^- \cdot \text{C}_6\text{H}_6\text{N}_4\text{O} \cdot 2\text{H}_2\text{O}$   
 $M_r = 466.84$   
 Monoclinic,  $P2_1/c$   
 $a = 8.6082$  (8) Å  
 $b = 14.7723$  (14) Å  
 $c = 16.8079$  (17) Å  
 $\beta = 104.609$  (2)°

$V = 2068.2$  (3) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.24$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.42 \times 0.38 \times 0.13$  mm

## Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{\min} = 0.764$ ,  $T_{\max} = 0.969$

12883 measured reflections  
 4653 independent reflections  
 3687 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.152$   
 $S = 1.03$   
 4653 reflections  
 302 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.37$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D–H \cdots A$                                  | $D–H$    | $H \cdots A$ | $D \cdots A$ | $D–H \cdots A$ |
|---|----------|--------------|--------------|----------------|
| $\text{N4}–\text{H4} \cdots \text{O2W}$         | 0.86     | 1.89         | 2.743 (2)    | 173            |
| $\text{N4P}–\text{H4P} \cdots \text{O1W}$       | 0.86     | 1.84         | 2.699 (3)    | 175            |
| $\text{O1W}–\text{H11W} \cdots \text{O7}^i$     | 0.82 (1) | 1.96 (2)     | 2.733 (3)    | 158 (3)        |
| $\text{O1W}–\text{H12W} \cdots \text{O2W}^{ii}$ | 0.82 (1) | 2.10 (1)     | 2.913 (3)    | 173 (3)        |
| $\text{O2W}–\text{H21W} \cdots \text{O3}^{iii}$ | 0.82 (1) | 2.09 (1)     | 2.875 (3)    | 162 (3)        |
| $\text{O2W}–\text{H22W} \cdots \text{N7P}^{iv}$ | 0.82 (1) | 1.96 (1)     | 2.771 (3)    | 177 (3)        |

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

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Xtal\_GX (Hall & du Boulay, 1997); software used to prepare material for publication: SHELXL97.

We acknowledge financial support from the Spanish Ministerio de Ciencia y Tecnología (project CTQ2008–00037/PPQ) and from the Junta de Andalucía (research group FQM 195). ABC is grateful for a FPU grant from the Spanish Ministerio de Educación y Ciencia.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2981).

## References

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Shang, R.-L., Du, L. & Sun, B.-W. (2006). *Acta Cryst.* **E62**, o2920–o2921.

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**supplementary materials**

*Acta Cryst.* (2010). E66, o459-o460 [ doi:10.1107/S1600536810002564 ]

## 4,7-Phenanthroline perchlorate-5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one-water (1/1/2)

A. B. Caballero, M. Quirós and J. M. Salas

### Comment

The title compound was obtained as a by-product when trying to synthesize a copper complex containing both heterocycles, as indicated in the preparation section. The formula of the compound is (47phenH)(HmtpO)(ClO<sub>4</sub>).2H<sub>2</sub>O (47phen = 4,7-phenanthroline and HmtpO = 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine-7(4*H*)-one), which also correspond to the contents of the asymmetric unit which is shown in Figure 1. The geometrical parameters of both heterocycles do not significantly differ from other compounds with protonated 47phen (Shang *et al.*, 2006, Gillard *et al.*, 1998) or neutral HmtpO (Navarro *et al.*, 1997, Salas *et al.* 1996). The species are linked in the crystal mainly by hydrogen bonds, water molecules being the main actors of the H-bond network. One of the independent water molecules (O1W) accepts an H-bond from the extra proton of 47phen (N4P—H) and donates towards the carbonyl O-atom (O7) of the triazolopyrimidine moiety and towards the other water molecule (O2W). The later also accepts an H-bond from the acidic H-atom of HmtpO (N4—H) acting as donor for the perchlorate anion and for the non-protonated N atom of 47phen (N7P). This builds a two-dimensional hydrogen bond network, which includes, among other motifs, centrosymmetric (HmtpO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> boxes, with both HmtpO molecules stacked with a separation of 3.4 Å and linked by two chains with two water molecules each, starting at N4P of one of the heterocycles and ending at O7 of the other: N4P—H···O1W—H···O2W—H···O7.

### Experimental

The compound was fortuitously obtained as a by-product when trying to synthesize a ternary complex of Cu(II) with 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine-7(4*H*)-one (HmtpO) and 4,7-phenanthroline (47phen). An aqueous solution (10 ml.) of Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0,75 g, 2 mmol), another aqueous solution (20 ml.) of HmtpO (0,61 g, 4 mmol) and an ethanolic solution (10 ml.) of 47phen (0,73 g, 4 mmol) were mixed and the mixture was refluxed for 2 h, a green precipitate (a Cu-Hmtpo complex) appearing which was filtered off. The mother liquor was left to stand at room temperature for two weeks, when a mixture of green and pale yellow crystals was obtained, which was filtered off. It was possible to separate both types of crystals under a lens, the green crystals turning out to be a Cu-phen complex whereas the pale yellow ones are the title compound, the structure of which is presented in this article. Elemental analysis data for C<sub>18</sub>H<sub>19</sub>ClN<sub>6</sub>O<sub>7</sub>. % Found (Calc.): C 46.17 (46.31), H 4.52 (4.10), N 17.79 (18.00).

### Refinement

Hydrogen atoms of the organic moieties were idealized with distances to their parent atoms of 0.93 (C) or 0.86 (N) Å, the location of acidic (N—H) H atoms being obvious from previous ΔF maps. Free rotation was allowed for the methyl group. Water hydrogen atoms were easily located in ΔF maps and refined with restrained O—H distances (0.82 (1) Å). Displacement parameters of all H atoms were fixed at 1.2 times the *U*<sub>eq</sub> of their parent atoms.

## Figures

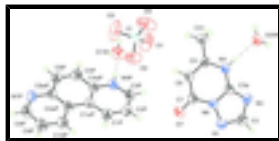


Fig. 1. View of the asymmetric unit of the title compound with the displacement ellipsoids shown at the 50% probability level. Hydrogen bonds are shown as dashed lines.

## 4,7-Phenanthroline perchlorate–5-methyl-1,2,4-triazolo[1,5-a]pyrimidin-7(4H)-one– water (1/1/2)

### Crystal data

$C_{12}H_9N_2^+ \cdot ClO_4^- \cdot C_6H_6N_4O \cdot 2H_2O$

$M_r = 466.84$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 8.6082\ (8)\ \text{\AA}$

$b = 14.7723\ (14)\ \text{\AA}$

$c = 16.8079\ (17)\ \text{\AA}$

$\beta = 104.609\ (2)^\circ$

$V = 2068.2\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 968$

$D_x = 1.499\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3841 reflections

$\theta = 2.4\text{--}24.6^\circ$

$\mu = 0.24\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Irregular, pale yellow

$0.42 \times 0.38 \times 0.13\ \text{mm}$

### Data collection

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

Detector resolution:  $8.26\ \text{pixels mm}^{-1}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 1999)

$T_{\min} = 0.764$ ,  $T_{\max} = 0.969$

12883 measured reflections

4653 independent reflections

3687 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 1.9^\circ$

$h = -11 \rightarrow 11$

$k = -18 \rightarrow 16$

$l = -22 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.152$

$S = 1.03$

4653 reflections

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and  
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.080P)^2 + 0.7P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

302 parameters

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

4 restraints

$$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

|      | <i>x</i>    | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|--------------|--------------|----------------------------------|
| Cl   | 0.45313 (6) | 0.33264 (4)  | 0.31768 (3)  | 0.04631 (18)                     |
| O1   | 0.3034 (3)  | 0.31480 (17) | 0.33511 (15) | 0.0894 (7)                       |
| O2   | 0.4656 (3)  | 0.42667 (14) | 0.30285 (15) | 0.0838 (6)                       |
| O3   | 0.4615 (4)  | 0.28347 (18) | 0.24717 (16) | 0.1138 (10)                      |
| O4   | 0.5784 (3)  | 0.30880 (19) | 0.38506 (17) | 0.1111 (9)                       |
| N1   | 0.0430 (2)  | 0.68226 (12) | 0.53673 (12) | 0.0482 (5)                       |
| C2   | 0.0189 (3)  | 0.67004 (16) | 0.61003 (16) | 0.0521 (6)                       |
| H2   | -0.0348     | 0.7130       | 0.6336       | 0.063*                           |
| N3   | 0.0760 (2)  | 0.59263 (13) | 0.65035 (12) | 0.0470 (4)                       |
| C3A  | 0.1429 (2)  | 0.55371 (13) | 0.59692 (12) | 0.0372 (4)                       |
| N4   | 0.2222 (2)  | 0.47442 (11) | 0.60339 (10) | 0.0390 (4)                       |
| H4   | 0.2287      | 0.4404       | 0.6456       | 0.047*                           |
| C5   | 0.2917 (3)  | 0.44833 (14) | 0.54280 (13) | 0.0416 (5)                       |
| C51  | 0.3840 (3)  | 0.36204 (17) | 0.55767 (17) | 0.0591 (6)                       |
| H51  | 0.4143      | 0.3444       | 0.5087       | 0.071*                           |
| H52  | 0.3184      | 0.3156       | 0.5725       | 0.071*                           |
| H53  | 0.4786      | 0.3704       | 0.6016       | 0.071*                           |
| C6   | 0.2757 (3)  | 0.49988 (15) | 0.47456 (13) | 0.0456 (5)                       |
| H6   | 0.3213      | 0.4791       | 0.4334       | 0.055*                           |
| C7   | 0.1924 (3)  | 0.58373 (15) | 0.46251 (13) | 0.0438 (5)                       |
| O7   | 0.1771 (2)  | 0.63513 (13) | 0.40383 (10) | 0.0629 (5)                       |
| N8   | 0.1250 (2)  | 0.60466 (11) | 0.52801 (10) | 0.0375 (4)                       |
| C1P  | 0.2195 (3)  | 0.60343 (16) | 0.13977 (14) | 0.0509 (6)                       |
| H1P  | 0.2555      | 0.6615       | 0.1325       | 0.061*                           |
| C1AP | 0.2186 (2)  | 0.53636 (14) | 0.08008 (12) | 0.0388 (4)                       |
| C2P  | 0.1672 (3)  | 0.58385 (19) | 0.20817 (15) | 0.0608 (7)                       |
| H2P  | 0.1682      | 0.6283       | 0.2475       | 0.073*                           |
| C3P  | 0.1126 (3)  | 0.49785 (19) | 0.21863 (15) | 0.0565 (6)                       |
| H3P  | 0.0758      | 0.4847       | 0.2648       | 0.068*                           |
| N4P  | 0.1128 (2)  | 0.43452 (14) | 0.16298 (11) | 0.0480 (5)                       |

## supplementary materials

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|      |            |              |               |            |
|------|------------|--------------|---------------|------------|
| H4P  | 0.0784     | 0.3814       | 0.1707        | 0.058*     |
| C4AP | 0.1650 (2) | 0.44961 (14) | 0.09408 (13)  | 0.0401 (5) |
| C5P  | 0.1638 (3) | 0.37718 (15) | 0.03805 (14)  | 0.0488 (5) |
| H5P  | 0.1270     | 0.3202       | 0.0482        | 0.059*     |
| C6P  | 0.2157 (3) | 0.39210 (15) | -0.02966 (14) | 0.0501 (5) |
| H6P  | 0.2193     | 0.3440       | -0.0648       | 0.060*     |
| C6AP | 0.2661 (2) | 0.47963 (15) | -0.04881 (13) | 0.0423 (5) |
| N7P  | 0.3086 (3) | 0.48934 (14) | -0.12090 (12) | 0.0548 (5) |
| C8P  | 0.3516 (3) | 0.57049 (19) | -0.14009 (16) | 0.0611 (7) |
| H8P  | 0.3800     | 0.5776       | -0.1896       | 0.073*     |
| C9P  | 0.3551 (3) | 0.64575 (18) | -0.09078 (16) | 0.0617 (7) |
| H9P  | 0.3864     | 0.7016       | -0.1071       | 0.074*     |
| C10P | 0.3139 (3) | 0.63783 (17) | -0.01789 (15) | 0.0539 (6) |
| H10P | 0.3155     | 0.6880       | 0.0157        | 0.065*     |
| C0AP | 0.2681 (2) | 0.55214 (14) | 0.00543 (13)  | 0.0397 (5) |
| O1W  | 0.0223 (2) | 0.26333 (13) | 0.18493 (13)  | 0.0679 (5) |
| H11W | -0.045 (3) | 0.237 (2)    | 0.1499 (15)   | 0.081*     |
| H12W | 0.095 (3)  | 0.2279 (18)  | 0.2039 (19)   | 0.081*     |
| O2W  | 0.2656 (3) | 0.37456 (12) | 0.74489 (11)  | 0.0640 (5) |
| H21W | 0.335 (3)  | 0.3355 (16)  | 0.7542 (19)   | 0.077*     |
| H22W | 0.275 (4)  | 0.4077 (17)  | 0.7846 (13)   | 0.077*     |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| Cl   | 0.0445 (3)  | 0.0470 (3)  | 0.0486 (3)  | -0.0056 (2)  | 0.0139 (2)   | -0.0066 (2)  |
| O1   | 0.0712 (13) | 0.1078 (18) | 0.1028 (18) | -0.0295 (12) | 0.0472 (13)  | -0.0301 (14) |
| O2   | 0.0952 (16) | 0.0500 (11) | 0.1048 (17) | -0.0044 (10) | 0.0228 (14)  | 0.0031 (11)  |
| O3   | 0.171 (3)   | 0.0986 (18) | 0.1052 (18) | -0.0598 (18) | 0.0961 (19)  | -0.0507 (15) |
| O4   | 0.0844 (17) | 0.1027 (19) | 0.120 (2)   | 0.0050 (14)  | -0.0229 (15) | 0.0294 (16)  |
| N1   | 0.0501 (11) | 0.0397 (10) | 0.0580 (12) | 0.0076 (8)   | 0.0193 (9)   | 0.0062 (8)   |
| C2   | 0.0545 (13) | 0.0445 (12) | 0.0642 (15) | 0.0067 (10)  | 0.0273 (12)  | -0.0001 (11) |
| N3   | 0.0546 (11) | 0.0445 (10) | 0.0475 (11) | 0.0028 (8)   | 0.0232 (9)   | 0.0028 (8)   |
| C3A  | 0.0364 (10) | 0.0377 (10) | 0.0383 (10) | -0.0050 (8)  | 0.0109 (8)   | 0.0017 (8)   |
| N4   | 0.0458 (9)  | 0.0350 (9)  | 0.0354 (9)  | 0.0014 (7)   | 0.0089 (7)   | 0.0048 (7)   |
| C5   | 0.0440 (11) | 0.0378 (11) | 0.0431 (11) | 0.0009 (9)   | 0.0110 (9)   | -0.0030 (9)  |
| C51  | 0.0713 (16) | 0.0464 (13) | 0.0624 (15) | 0.0156 (12)  | 0.0223 (13)  | 0.0041 (12)  |
| C6   | 0.0550 (13) | 0.0458 (12) | 0.0388 (11) | 0.0042 (10)  | 0.0174 (10)  | -0.0018 (9)  |
| C7   | 0.0468 (11) | 0.0483 (12) | 0.0363 (11) | 0.0011 (9)   | 0.0109 (9)   | 0.0023 (9)   |
| O7   | 0.0826 (13) | 0.0654 (11) | 0.0457 (9)  | 0.0198 (9)   | 0.0254 (9)   | 0.0208 (8)   |
| N8   | 0.0400 (9)  | 0.0337 (8)  | 0.0385 (9)  | 0.0012 (7)   | 0.0094 (7)   | 0.0034 (7)   |
| C1P  | 0.0661 (15) | 0.0418 (12) | 0.0479 (13) | 0.0001 (11)  | 0.0200 (11)  | -0.0025 (10) |
| C1AP | 0.0404 (10) | 0.0384 (11) | 0.0378 (11) | 0.0008 (8)   | 0.0101 (9)   | 0.0010 (8)   |
| C2P  | 0.0820 (18) | 0.0600 (15) | 0.0460 (13) | 0.0092 (13)  | 0.0266 (13)  | -0.0063 (12) |
| C3P  | 0.0645 (15) | 0.0705 (17) | 0.0407 (12) | 0.0067 (13)  | 0.0250 (11)  | 0.0086 (12)  |
| N4P  | 0.0493 (10) | 0.0505 (11) | 0.0458 (11) | -0.0016 (8)  | 0.0153 (8)   | 0.0108 (9)   |
| C4AP | 0.0383 (10) | 0.0419 (11) | 0.0396 (11) | 0.0020 (8)   | 0.0090 (9)   | 0.0051 (9)   |
| C5P  | 0.0572 (13) | 0.0363 (11) | 0.0530 (13) | -0.0077 (10) | 0.0140 (11)  | 0.0004 (10)  |

|      |             |             |             |              |             |              |
|------|-------------|-------------|-------------|--------------|-------------|--------------|
| C6P  | 0.0644 (14) | 0.0394 (12) | 0.0474 (13) | -0.0040 (10) | 0.0157 (11) | -0.0078 (10) |
| C6AP | 0.0454 (11) | 0.0429 (11) | 0.0396 (11) | -0.0017 (9)  | 0.0127 (9)  | -0.0007 (9)  |
| N7P  | 0.0691 (13) | 0.0574 (12) | 0.0421 (11) | -0.0034 (10) | 0.0217 (10) | -0.0055 (9)  |
| C8P  | 0.0750 (17) | 0.0690 (17) | 0.0456 (13) | -0.0101 (14) | 0.0271 (13) | 0.0053 (12)  |
| C9P  | 0.0794 (18) | 0.0540 (14) | 0.0570 (15) | -0.0140 (13) | 0.0271 (14) | 0.0073 (12)  |
| C10P | 0.0715 (16) | 0.0418 (12) | 0.0513 (13) | -0.0093 (11) | 0.0210 (12) | -0.0009 (10) |
| C0AP | 0.0405 (10) | 0.0399 (11) | 0.0390 (11) | -0.0018 (8)  | 0.0106 (9)  | -0.0001 (9)  |
| O1W  | 0.0710 (13) | 0.0532 (11) | 0.0702 (13) | -0.0163 (9)  | 0.0007 (10) | 0.0043 (9)   |
| O2W  | 0.1006 (15) | 0.0453 (10) | 0.0443 (10) | 0.0124 (10)  | 0.0149 (10) | 0.0037 (8)   |

*Geometric parameters (Å, °)*

|           |             |                |             |
|-----------|-------------|----------------|-------------|
| Cl—O4     | 1.398 (2)   | C1AP—C0AP      | 1.442 (3)   |
| Cl—O3     | 1.407 (2)   | C2P—C3P        | 1.381 (4)   |
| Cl—O1     | 1.416 (2)   | C2P—H2P        | 0.9300      |
| Cl—O2     | 1.420 (2)   | C3P—N4P        | 1.323 (3)   |
| N1—C2     | 1.313 (3)   | C3P—H3P        | 0.9300      |
| N1—N8     | 1.374 (2)   | N4P—C4AP       | 1.362 (3)   |
| C2—N3     | 1.357 (3)   | N4P—H4P        | 0.8600      |
| C2—H2     | 0.9300      | C4AP—C5P       | 1.424 (3)   |
| N3—C3A    | 1.315 (3)   | C5P—C6P        | 1.341 (3)   |
| C3A—N4    | 1.346 (3)   | C5P—H5P        | 0.9300      |
| C3A—N8    | 1.357 (3)   | C6P—C6AP       | 1.426 (3)   |
| N4—C5     | 1.361 (3)   | C6P—H6P        | 0.9300      |
| N4—H4     | 0.8600      | C6AP—N7P       | 1.359 (3)   |
| C5—C6     | 1.354 (3)   | C6AP—C0AP      | 1.404 (3)   |
| C5—C51    | 1.489 (3)   | N7P—C8P        | 1.318 (3)   |
| C51—H51   | 0.9600      | C8P—C9P        | 1.382 (4)   |
| C51—H52   | 0.9600      | C8P—H8P        | 0.9300      |
| C51—H53   | 0.9600      | C9P—C10P       | 1.364 (3)   |
| C6—C7     | 1.420 (3)   | C9P—H9P        | 0.9300      |
| C6—H6     | 0.9300      | C10P—C0AP      | 1.411 (3)   |
| C7—O7     | 1.225 (3)   | C10P—H10P      | 0.9300      |
| C7—N8     | 1.402 (3)   | O1W—H11W       | 0.816 (10)  |
| C1P—C2P   | 1.367 (3)   | O1W—H12W       | 0.819 (10)  |
| C1P—C1AP  | 1.409 (3)   | O2W—H21W       | 0.818 (10)  |
| C1P—H1P   | 0.9300      | O2W—H22W       | 0.816 (10)  |
| C1AP—C4AP | 1.402 (3)   |                |             |
| O4—Cl—O3  | 111.1 (2)   | C4AP—C1AP—C0AP | 118.41 (19) |
| O4—Cl—O1  | 110.00 (17) | C1P—C1AP—C0AP  | 123.79 (19) |
| O3—Cl—O1  | 108.70 (14) | C1P—C2P—C3P    | 119.8 (2)   |
| O4—Cl—O2  | 108.15 (15) | C1P—C2P—H2P    | 120.1       |
| O3—Cl—O2  | 109.56 (15) | C3P—C2P—H2P    | 120.1       |
| O1—Cl—O2  | 109.35 (15) | N4P—C3P—C2P    | 119.9 (2)   |
| C2—N1—N8  | 101.11 (17) | N4P—C3P—H3P    | 120.3       |
| N1—C2—N3  | 117.5 (2)   | C2P—C3P—H3P    | 119.8       |
| N1—C2—H2  | 121.3       | C3P—N4P—C4AP   | 123.0 (2)   |
| N3—C2—H2  | 121.2       | C3P—N4P—H4P    | 118.5       |
| C3A—N3—C2 | 101.16 (18) | C4AP—N4P—H4P   | 118.5       |



## supplementary materials

|               |             |                |             |
|---------------|-------------|----------------|-------------|
| N3—C3A—N4     | 128.72 (19) | N4P—C4AP—C1AP  | 119.04 (19) |
| N3—C3A—N8     | 111.43 (18) | N4P—C4AP—C5P   | 119.39 (19) |
| N4—C3A—N8     | 119.85 (17) | C1AP—C4AP—C5P  | 121.57 (19) |
| C3A—N4—C5     | 119.71 (17) | C6P—C5P—C4AP   | 119.3 (2)   |
| C3A—N4—H4     | 120.1       | C6P—C5P—H5P    | 120.4       |
| C5—N4—H4      | 120.2       | C4AP—C5P—H5P   | 120.3       |
| C6—C5—N4      | 120.29 (19) | C5P—C6P—C6AP   | 121.7 (2)   |
| C6—C5—C51     | 124.0 (2)   | C5P—C6P—H6P    | 119.0       |
| N4—C5—C51     | 115.68 (19) | C6AP—C6P—H6P   | 119.2       |
| C5—C51—H51    | 109.7       | N7P—C6AP—C0AP  | 122.4 (2)   |
| C5—C51—H52    | 109.4       | N7P—C6AP—C6P   | 117.6 (2)   |
| H51—C51—H52   | 109.5       | C0AP—C6AP—C6P  | 119.99 (19) |
| C5—C51—H53    | 109.4       | C8P—N7P—C6AP   | 118.0 (2)   |
| H51—C51—H53   | 109.5       | N7P—C8P—C9P    | 123.3 (2)   |
| H52—C51—H53   | 109.5       | N7P—C8P—H8P    | 118.3       |
| C5—C6—C7      | 123.46 (19) | C9P—C8P—H8P    | 118.3       |
| C5—C6—H6      | 118.2       | C10P—C9P—C8P   | 119.9 (2)   |
| C7—C6—H6      | 118.3       | C10P—C9P—H9P   | 120.1       |
| O7—C7—N8      | 120.9 (2)   | C8P—C9P—H9P    | 120.0       |
| O7—C7—C6      | 127.1 (2)   | C9P—C10P—C0AP  | 118.7 (2)   |
| N8—C7—C6      | 111.98 (18) | C9P—C10P—H10P  | 120.6       |
| C3A—N8—N1     | 108.82 (16) | C0AP—C10P—H10P | 120.6       |
| C3A—N8—C7     | 124.57 (17) | C6AP—C0AP—C10P | 117.58 (19) |
| N1—N8—C7      | 126.40 (17) | C6AP—C0AP—C1AP | 118.92 (19) |
| C2P—C1P—C1AP  | 120.4 (2)   | C10P—C0AP—C1AP | 123.5 (2)   |
| C2P—C1P—H1P   | 119.8       | H11W—O1W—H12W  | 108 (3)     |
| C1AP—C1P—H1P  | 119.8       | H21W—O2W—H22W  | 111 (3)     |
| C4AP—C1AP—C1P | 117.80 (19) |                |             |

### 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> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| N4—H4...O2W                  | 0.86        | 1.89          | 2.743 (2)             | 173                     |
| N4P—H4P...O1W                | 0.86        | 1.84          | 2.699 (3)             | 175                     |
| O1W—H11W...O7 <sup>i</sup>   | 0.82 (1)    | 1.96 (2)      | 2.733 (3)             | 158 (3)                 |
| O1W—H12W...O2W <sup>ii</sup> | 0.82 (1)    | 2.10 (1)      | 2.913 (3)             | 173 (3)                 |
| O2W—H21W...O3 <sup>iii</sup> | 0.82 (1)    | 2.09 (1)      | 2.875 (3)             | 162 (3)                 |
| O2W—H22W...N7P <sup>iv</sup> | 0.82 (1)    | 1.96 (1)      | 2.771 (3)             | 177 (3)                 |

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

Fig. 1

