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Different nucleobase orientations in two cyclic 2′,3′-phosphates of purine ribonucleosides: Et_3NH(2′,3′-cAMP) and Et_3NH(2′,3′-cGMP)·H_2O

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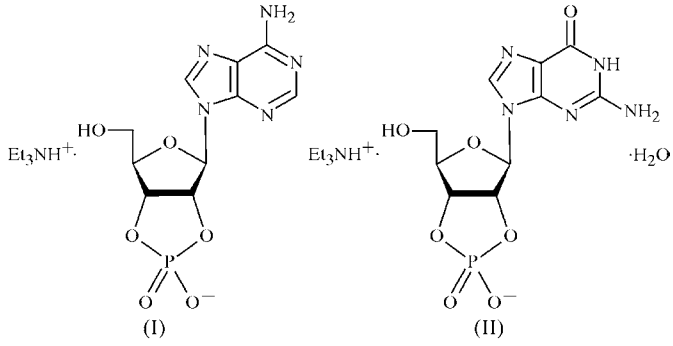
The crystal structures of triethylammonium adenosine cyclic 2′,3′-phosphate {systematic name: triethylammonium 4-(6-aminopurin-9-yl)-6-hydroxymethyl-2-oxido-2-oxoperhydrofurano[3,4-*c*][1,3,2]dioxaphosphole}, Et_3NH(2′,3′-cAMP) or $C_6H_{16}N^+\cdot C_{10}H_{11}N_5O_6P^-$, (I), and guanosine cyclic 2′,3′-phosphate monohydrate {systematic name: triethylammonium 6-hydroxymethyl-2-oxido-2-oxo-4-(6-oxo-1,6-dihydropurin-9-yl)perhydrofurano[3,4-*c*][1,3,2]dioxaphosphole monohydrate}, [Et_3NH(2′,3′-cGMP)]·H_2O or $C_6H_{16}N^+\cdot C_{10}H_{11}N_5O_7P^-\cdot H_2O$, (II), reveal different nucleobase orientations, *viz.* *anti* in (I) and *syn* in (II). These are stabilized by different inter- and intramolecular hydrogen bonds. The structures also exhibit different ribose ring puckering [$_4E$ in (I) and $^3T_2$ in (II)] and slightly different 1,3,2-dioxaphospholane ring conformations, *viz.* envelope with atom C2′ in (I) and C3′ in (II) puckered. Infinite ribbons of 2′,3′-cAMP$^-$ and helical chains of 2′,3′-cGMP$^-$ ions, both formed by O—H···O, N—H···*X* and C—H···*X* (*X* = O or N) hydrogen-bond contacts, characterize (I) and (II), respectively.

Comment

The title ribonucleoside cyclic 2′,3′-phosphates, *viz.* triethylammonium adenosine cyclic 2′,3′-phosphate, Et_3NH-(2′,3′-cAMP), (I), and guanosine cyclic 2′,3′-phosphate



monohydrate, [Et_3NH(2′,3′-cGMP)]·H_2O, (II), are intermediates of RNA degradation (Raines, 1998; Kuimelis & McLaughlin, 1998; Oivanen *et al.*, 1998). The mechanisms of the two steps of this ribonuclease-catalyzed process, *viz.* (i) transphosphorylation giving the respective nucleoside cyclic 2′,3′-phosphate and (ii) its hydrolysis (by the same enzyme) towards the nucleoside 3′-phosphate, are well recognized. However, accumulation of the respective nucleoside cyclic

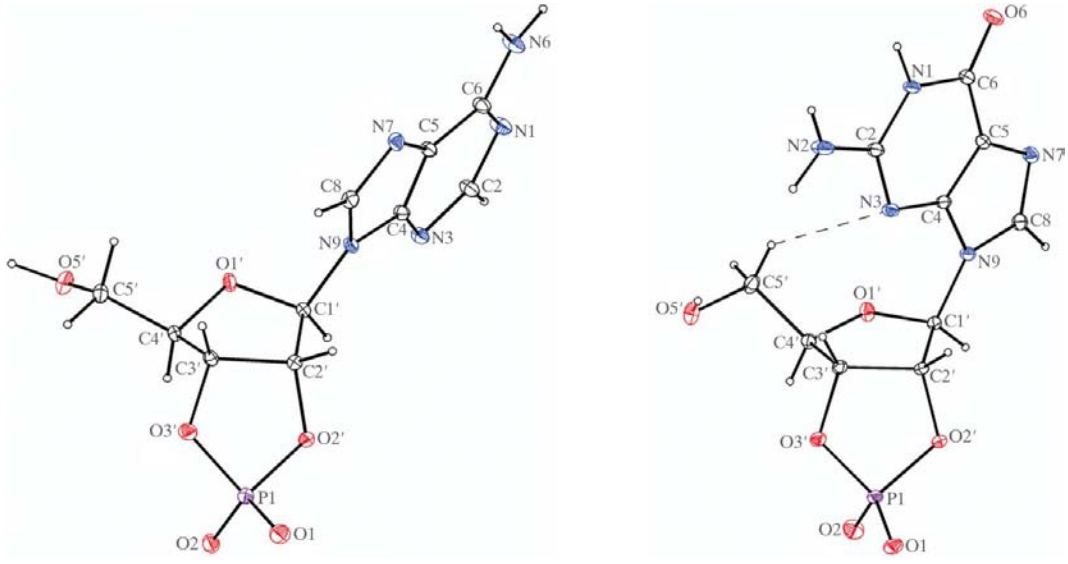


Figure 1
The molecular structure of the 2′,3′-cAMP$^-$ (left) and 2′,3′-cGMP$^-$ (right) anions in (I) and (II), respectively, showing the atom-numbering schemes and the intramolecular C—H···N hydrogen bond in (II) (marked with a dashed line). Displacement ellipsoids are drawn at the 20% probability level for the non-H atoms.

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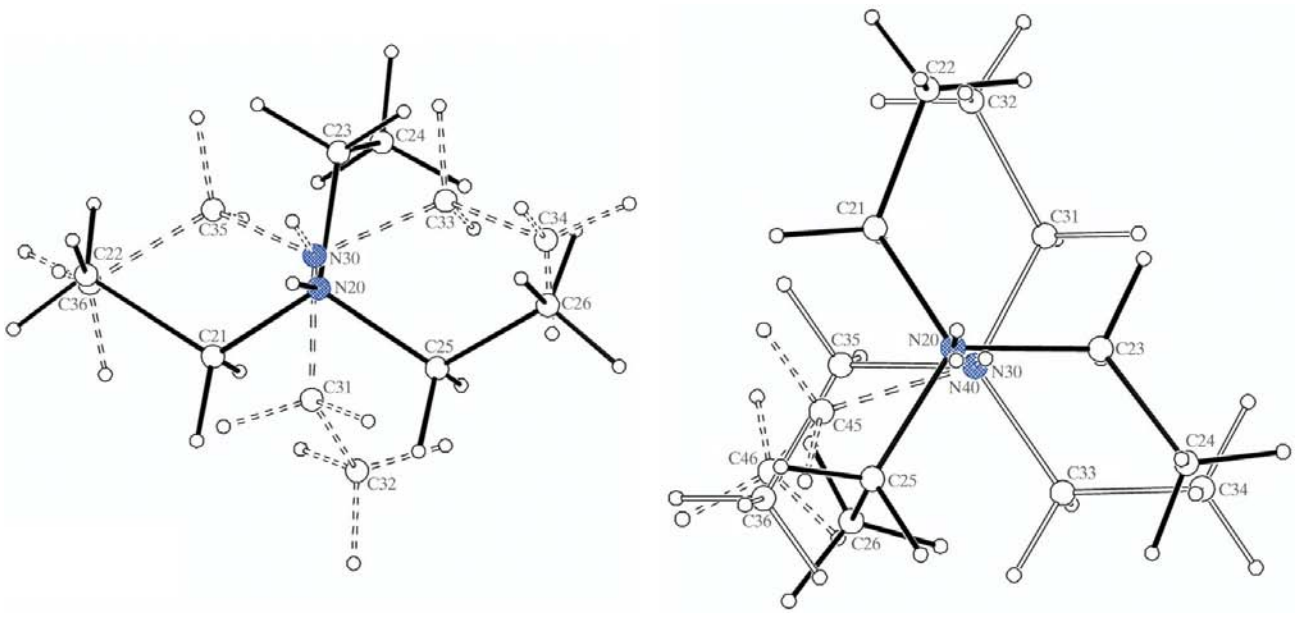

Figure 2
The molecular structure of the disordered triethylammonium cations in (I) [left; site-occupancy factors 0.830 (5) (solid line) and 0.170 (5) (double-dashed line)] and (II) [right; site-occupancy factors 0.698 (3) (solid), 0.191 (5) (open) and 0.111 (5) (double-dashed line)]. Atoms are shown as circles of arbitrary radii.

2′,3′-phosphates has been observed during degradation of the RNA chain, which makes the reasons for the different kinetics of the above steps intriguing (Cuchillo *et al.*, 1993). The fact is that nucleoside cyclic 2′,3′-phosphates are chemically less stable than linear dinucleoside phosphates (Thompson *et al.*, 1994). Thus, there must be another cause of the kinetic advantage of enzymatic transphosphorylation of RNA over hydrolysis of the produced nucleoside cyclic 2′,3′-phosphates. Since enzyme-catalyzed reactions are involved it might be acceptable to postulate that linear (3′–5′) dinucleoside phosphates have different conformations compared with their cyclic 2′,3′-analogues. In consequence, the latter form might give a less productive complex with the enzyme. If this is the case, the crystal structures of nucleoside cyclic 2′,3′-phosphates become of high importance in the verification of the above postulates.

Nucleoside cyclic 2′,3′-phosphates have been poorly explored as regards their solid-state structures. The only X-ray data so far deposited with the Cambridge Structural Database (CSD; Allen, 2002), *viz.* two pyrimidine nucleotides [2′,3′-cCMP (Reddy & Saenger, 1978; CSD refcode CYCYPH10) and Na(2′,3′-cCMP) (Coulter, 1973; CSD refcode CYTCYP20)] and one uridine phosphorothioate analogue [Et_3NH(2′,3′-cUMPS) (URIDPS10; Saenger & Eckstein, 1970)], do not reveal any correlations between the nucleobase type or the chemical environment and the molecular structure observed in the crystal. In particular, no such influence on nucleobase orientation, ribose puckering or 1,3,2-dioxaphospholane ring conformation has been observed. The purine cyclic 2′,3′-phosphates have never been crystallized and structurally characterized by X-ray crystallography.

We report here the results of our single-crystal X-ray study of the two title cyclic 2′,3′-phosphates of purine ribonucleosides in the form of their triethylammonium salts, (I) and (II), and compare the results with those previously described for the three above-mentioned analogous pyrimidine compounds.

The compounds presented here crystallize with one 2′,3′-cyclic nucleotide anion (Fig. 1), one Et_3NH^+ cation [disordered in both (I) and (II); Fig. 2] and one water molecule [for (II)] in the asymmetric unit. The 2′,3′-cAMP$^-$ ion in (I) and 2′,3′-cGMP$^-$ in (II) reveal different orientations of the nucleobase with respect to the ribose ring. This fact is reflected in the conformation about the glycosidic (C1′—N9) bond, which is *anti* in (I) and *syn* in (II), and gives rise to different values of the χ_{CN} angle (O1′—C1′—N9—C4; see Tables 1 and 3). Most nucleosides and nucleotides show a preference for the *anti* conformation about the glycosidic bond in the crystalline state; however, some of the cyclic nucleotides, *e.g.* 2′,3′-cCMP in its sodium salt, 3′,5′-cAMP and 3′,5′-cGMP, exist in the *syn* conformation (Coulter, 1973; Sundaralingam, 1969; Allen, 2002). Surprisingly, 2′,3′-cCMP in the form of the free acid and its sodium salt crystallize with a different conformation about the χ_{CN} bond, *viz. anti* and *syn*, respectively (Reddy & Saenger, 1978; Coulter, 1973).

The different orientation of the nucleobase with respect to the ribose ring observed in the 2′,3′-cAMP$^-$ and 2′,3′-cGMP$^-$ anions is accompanied by a different ribose ring puckering. Although the conformation of the sugar moiety of the cyclic 2′,3′-phosphates may be described by the use of the classical conformational descriptors for envelope and twist puckering, the presence of another cyclic system (O/P/O/C/C) results in significant deformation, mainly flattening of the furanose ring. Therefore, the sugar conformations observed in (I) and (II) are distorted C4′-*exo* envelope ($_4E$) and C3′-*endo*,C2′-*exo* twist ($^3T_2$), respectively. The q_2 and Φ_2 (Cremer & Pople, 1975) puckering parameters are 0.354 (3) Å and 319.4 (5)° for (I),

and 0.165 (2) Å and 273.5 (5)° for (II). The puckered atom C4′ in the anion in (I) is displaced by about 0.54 Å from the four-atom plane of the sugar ring. The angle between the O1′/C4′/C3′ and O1′/C1′/C2′/C3′ planes is 36.0 (2)°. The distances of the puckered C3′ and C2′ atoms from the three-atom plane in the $^3T_2$ ribose ring in (II) are only about 0.16 and 0.11 Å, respectively. The conformations of the ribose rings observed in (I) and (II) differ from those previously observed in the related compounds described so far, *viz.* Na(2′,3′-cCMP) (Coulter, 1973) and Et_3NH(2′,3′-cUMPS) (Saenger & Eckstein, 1970), which show the ribose ring in an envelope conformation with O1′-*endo* or O1′-*exo* puckering, and also differ from the $^2T_3$ conformation observed in 2′,3′-cCMP (Reddy & Saenger, 1978).

The orientation of the ribose hydroxymethyl O5′ atom with respect to the sugar ring is also different in the cyclic 2′,3′-phosphates of purine ribonucleotides presented here. The differences are reflected in the conformation about the C4′—C5′ bond, which is *gauche–trans* for (I) and *trans–gauche* for (II) (see the O1′—C4′—C5′—O5′ and C3′—C4′—C5′—O5′ torsion angles in Tables 1 and 3). The previously reported data reveal the *gauche–trans* conformation for one of two crystallographically independent anions in Na(2′,3′-cCMP) and the *trans–gauche* conformation for Et_3NH(2′,3′-cUMPS). However, the conformation about the C4′—C5′ bond observed in the second anion in Na(2′,3′-cCMP) and in the acid 2′,3′-cCMP is *gauche–gauche*, which is also the commonly observed C4′—C5′ conformation in nucleosides, their phosphate monoesters and polinucleotides in the solid state (Sundaralingam, 1969; Allen, 2002).

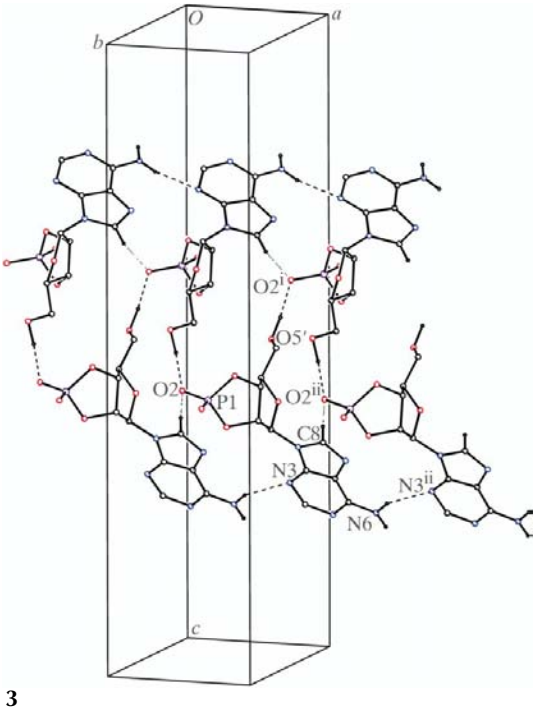

Figure 3
The arrangement of the 2′,3′-cAMP$^-$ anions in (I) within the ribbon formed by adjacent anions related by 2_1 and direct *a*-axis translation, linked by O—H···O, N—H···N (dashed lines) and C—H···O (dotted lines) interactions. H atoms not involved in these contacts are not shown. The symmetry codes are as given in Table 2.

The 1,3,2-dioxaphospholane ring (O/P/O/C/C) in both (I) and (II) exists in an envelope conformation, with atoms C2′ and C3′, respectively, displaced from the four-atom planes by about 0.41 and 0.31 Å, respectively. The mutual orientation of the two cyclic systems (the ribose and dioxaphospholane rings) can be described by the angle between the planes built up from three or four atoms of each ring. Thus, the angle between the O1′/C1′/C2′/C3′ and O2′/P1/O3′/C3′ planes in (I) is 47.4 (2)°, and that between the C4′/O1′/C1′ and C2′/O2′/P1/O3′ planes in (II) is 108.4 (2)°.

Significant deviation from the ideal tetrahedral geometry around the P atom is observed in both 2′,3′-cAMP$^-$ and 2′,3′-cGMP$^-$ anions. This deviation is mainly reflected in the values of the exocyclic O1—P1—O2 and the endocyclic O2′—P1—O3′ angles, which differ from one another by about 21°.

The crystal and molecular structures of (I) and (II) are stabilized by a network of O—H···*X* and N—H···*X* hydrogen bonds, and C—H···*X* close contacts (where *X* = O and N). Some of these bonds also stabilize the different orientation of the nucleobase with respect to the ribose ring observed in the 2′,3′-cAMP$^-$ and 2′,3′-cGMP$^-$ anions.

Adjacent symmetry-related anions in (I) are linked by O5′—H5′···O2^{i}, N6—H61···N3^{ii} and C8—H8···O2^{ii} interactions, in which hydroxymethyl, phosphate and nucleobase groups are involved (the geometry and symmetry codes are listed in Table 2). Such a combination of direct *a*-axis translation [generating $R_2^2(15)$ ring motifs] and [100] screw rotation [resulting in $R_3^2(18)$ rings] gives rise to infinite ribbons of anions parallel to the *a* axis, shown in Fig. 3. It is noted that the ribbon-stabilizing intermolecular N—H···O and C—H···O contacts, in which the nucleobase acts as the donor, may also stabilize the *anti* orientation of the adenine moiety to the ribose ring. In the crystal structure of (I), every ribbon is connected to four adjacent ribbons by N—H···O and N—H···N hydrogen bonds. As a result, a three–dimensional hydrogen-bond network is formed. In the channels formed in this way, the Et_3NH^+ cations are located and linked with the anions by N20—H20···O1 interactions.

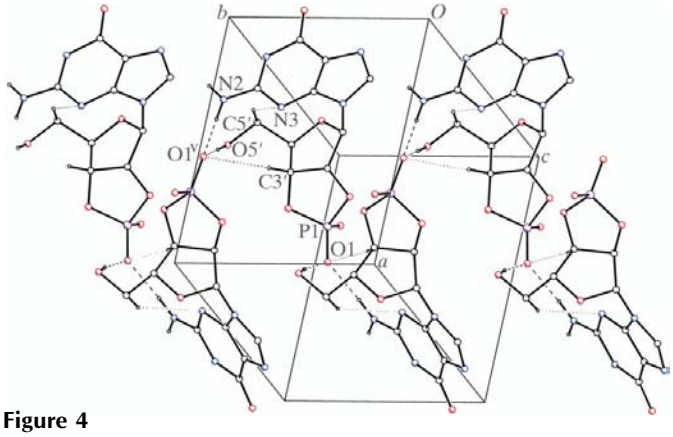

Figure 4
The arrangement of the 2′,3′-cGMP$^-$ anions in (II) within the helical chain formed by adjacent 2_1-related anions joined to one another by O—H···O, N—H···O (dashed lines) and C—H···N (dotted lines) interactions. H atoms not involved in these contacts are not shown. The symmetry code is as given in Table 4.

The crystal structure of (II) is built up from 2′,3′-cGMP$^-$ anions, Et_3NH^+ cations and water molecules. Adjacent 2_1-related anions are linked to one another by O—H···O, N—H···O and C—H···O interactions to form infinite helical chains along the *b* axis. As shown in Fig. 4 and Table 4, sugar atoms O5′ and C3′, as well as guanine atom N2 of one anion, act as the donors in these three intermolecular contacts, while only one phosphate O atom (O1) from the adjacent anion, is an acceptor. Hence, four-centered bonds stabilize the structure of the chains formed in the crystal of (II). It is possible that a rather weak intramolecular C5′—H52′···N3 interaction, accompanied by a moderately strong N2—H22···O1^{v} (see Table 4) interaction, may increase the stability of the *syn* conformation of the base with relation to the ribose ring of the 2′,3′-cGMP$^-$ anion.

Adjacent chains in the crystal structure of (II) are linked to one another by a three-centered hydrogen bond formed by N1—H1···O6^{vii} and N2—H21···O6^{vii} contacts (both having the common acceptor O6^{vii}; Table 4) and by the C8—H8···O1′^{viii} interaction. Additionally, the water molecules act as bridges between pairs of adjacent chains. The voids formed in this way between the chains, partly filled with the water molecules, are additionally occupied by Et_3NH^+ cations linked with the phosphate O atoms by N—H···O hydrogen bonds similar to those found in (I). This results in an extensive three-dimensional hydrogen-bond network.

In conclusion, the crystal and molecular structures of two purine 2′,3′-cyclic ribonucleotides (synthesized and crystallized in the form of their triethylammonium salts) have been described. The conformations observed in the 2′,3′-cAMP$^-$ and 2′,3′-cGMP$^-$ anions reveal significant differences, the most impressive being the different nucleobase orientation.

Experimental

Compounds (I) and (II) were synthesized according to previously described procedures (Jankowska *et al.*, 2000). Crystals were obtained by slow evaporation of 2-propanol/water or water/ethanol/methanol solutions of (I) and (II), respectively, at 280 K. The data for (II) were collected at 200 (2) K owing to weak reflections at *c**/3 and 2*c**/3 observed at lower temperature.

Compound (I)

Crystal data

$C_6H_{16}N^+\cdot C_{10}H_{11}N_5O_6P^-$
M_r = 430.41
Orthorhombic, $P2_12_12_1$
a = 6.704 (2) Å
b = 10.493 (3) Å
c = 28.536 (7) Å
V = 2007.4 (10) Å^3
Z = 4
D_x = 1.424 Mg m^{-3}
Cu *Kα* radiation
μ = 1.63 mm^{-1}
T = 100 (2) K
Needle, colorless
0.29 × 0.09 × 0.03 mm

Data collection

Xcalibur PX diffractometer with an Onyx CCD camera
ω and φ scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
T_{min} = 0.742, T_{max} = 0.954
14174 measured reflections
3911 independent reflections
3559 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 75.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.126
S = 1.09
3911 reflections
336 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.7467P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0018 (3)
Absolute structure: Flack (1983), 1481 Friedel pairs
Flack parameter: −0.02 (3)

Table 1
Selected geometric parameters (Å, °) for (I).

P1—O1	1.483 (2)	P1—O2′	1.623 (2)
P1—O2	1.484 (2)	P1—O3′	1.612 (2)
O1—P1—O2	118.2 (2)	O2—P1—O3′	111.0 (2)
O1—P1—O2′	110.0 (2)	O2′—P1—O3′	96.3 (1)
O1—P1—O3′	109.7 (2)	C2′—O2′—P1	111.7 (2)
O2—P1—O2′	109.5 (2)	C3′—O3′—P1	112.0 (2)
O1—P1—O2′—C2′	−98.9 (2)	O1′—C1′—C2′—O2′	109.2 (2)
O2—P1—O2′—C2′	129.7 (2)	O1′—C1′—C2′—C3′	−2.2 (3)
O3′—P1—O2′—C2′	14.7 (2)	O2′—C2′—C3′—O3′	28.5 (3)
O1—P1—O3′—C3′	117.7 (2)	C1′—C2′—C3′—O3′	143.2 (2)
O2—P1—O3′—C3′	−109.9 (2)	O2′—C2′—C3′—C4′	−91.6 (2)
O2′—P1—O3′—C3′	3.8 (2)	C1′—C2′—C3′—C4′	23.2 (3)
P1—O2′—C2′—C1′	−138.0 (2)	O3′—C3′—C4′—O1′	−152.0 (2)
P1—O2′—C2′—C3′	−26.9 (3)	C2′—C3′—C4′—O1′	−36.0 (3)
P1—O3′—C3′—C2′	−19.8 (3)	O1′—C4′—C5′—O5′	74.2 (3)
P1—O3′—C3′—C4′	94.0 (2)	C3′—C4′—C5′—O5′	−171.0 (2)
C4′—O1′—C1′—C2′	−21.5 (3)	O1′—C1′—N9—C8	74.1 (3)
C1′—O1′—C4′—C3′	36.2 (3)	O1′—C1′—N9—C4	−100.3 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5′—H5′···O2^{i}	1.05 (5)	1.72 (5)	2.772 (3)	174 (5)
N6—H61···N3^{ii}	0.86 (4)	2.19 (4)	2.957 (4)	149 (4)
N6—H62···O2′^{iii}	1.04 (5)	2.09 (5)	3.090 (3)	160 (4)
N20—H20···O1	0.93	1.74	2.660 (4)	168
C2′—H2′···N1^{iv}	1.02 (4)	2.49 (4)	3.341 (4)	140 (3)
C8—H8···O2^{ii}	1.03 (3)	2.25 (3)	3.260 (4)	168 (3)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x+1, y, z$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Compound (II)

Crystal data

$C_6H_{16}N^+\cdot C_{10}H_{11}N_5O_7P^-\cdot H_2O$
M_r = 464.42
Monoclinic, $P2_1$
a = 10.611 (3) Å
b = 7.931 (3) Å
c = 12.585 (3) Å
β = 96.89 (3)°
V = 1051.5 (6) Å^3
Z = 2
D_x = 1.467 Mg m^{-3}
Mo *Kα* radiation
μ = 0.19 mm^{-1}
T = 200 (2) K
Plate, colorless
0.60 × 0.40 × 0.15 mm

Data collection

Kuma KM-4 diffractometer with a Sapphire CCD camera
ω scans
21121 measured reflections
6943 independent reflections
5239 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 35.0°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.077$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
6943 reflections	Absolute structure: Flack (1983), 2054 Friedel pairs
369 parameters	Flack parameter: 0.08 (6)
H atoms treated by a mixture of independent and constrained refinement	

Table 3
Selected geometric parameters (Å, °) for (II).

P1—O1	1.4803 (12)	P1—O2′	1.6172 (12)
P1—O2	1.4872 (12)	P1—O3′	1.6040 (12)
O1—P1—O2	116.99 (7)	O2—P1—O3′	112.27 (7)
O1—P1—O3′	109.37 (7)	O2′—P1—O3′	96.94 (6)
O1—P1—O2′	111.47 (7)	C2′—O2′—P1	113.44 (10)
O2—P1—O2′	107.99 (7)	C3′—O3′—P1	112.07 (10)
O1—P1—O2′—C2′	−114.1 (1)	O1′—C1′—C2′—O2′	100.2 (2)
O2—P1—O2′—C2′	116.1 (1)	O1′—C1′—C2′—C3′	−13.2 (2)
O3′—P1—O2′—C2′	−0.1 (1)	O2′—C2′—C3′—O3′	20.3 (2)
O1—P1—O3′—C3′	129.1 (1)	C1′—C2′—C3′—O3′	135.5 (2)
O2—P1—O3′—C3′	−99.3 (1)	O2′—C2′—C3′—C4′	−98.7 (2)
O2′—P1—O3′—C3′	13.4 (1)	C1′—C2′—C3′—C4′	16.5 (2)
P1—O2′—C2′—C1′	−124.7 (1)	O3′—C3′—C4′—O1′	−130.0 (2)
P1—O2′—C2′—C3′	−11.9 (2)	C2′—C3′—C4′—O1′	−14.3 (2)
P1—O3′—C3′—C2′	−21.4 (2)	O1′—C4′—C5′—O5′	176.9 (2)
P1—O3′—C3′—C4′	93.1 (2)	C3′—C4′—C5′—O5′	−64.1 (2)
C4′—O1′—C1′—C2′	4.4 (2)	O1′—C1′—N9—C8	−98.8 (2)
C1′—O1′—C4′—C3′	6.4 (2)	O1′—C1′—N9—C4	65.2 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5′—H5′···O1^{v}	0.84 (3)	1.95 (3)	2.777 (2)	170 (3)
O*W*—H1*W*···O2	0.81 (3)	2.05 (3)	2.843 (2)	166 (3)
O*W*—H2*W*···N7^{vi}	0.93 (3)	2.09 (3)	3.011 (2)	174 (2)
N1—H1···O6^{vii}	0.91 (2)	2.13 (2)	2.860 (2)	137 (2)
N2—H21···O6^{vii}	0.79 (3)	2.33 (3)	2.985 (2)	141 (2)
N2—H22···O1^{v}	0.94 (2)	1.93 (2)	2.867 (2)	176 (2)
N20—H20···O2	0.93	1.76	2.656 (4)	162
C3′—H3′···O1^{v}	0.99 (2)	2.51 (2)	3.436 (2)	156 (2)
C5′—H52′···N3	0.94 (2)	2.63 (2)	3.406 (2)	139 (2)
C8—H8···O1′^{viii}	0.96 (2)	2.49 (2)	3.333 (2)	146 (2)

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

The Et_3NH^+ cations were disordered over two positions in (I) [with site-occupancy factors of 0.830 (5) for N20 and 0.170 (5) for N30] and over three positions in (II) [with site-occupancy factors of 0.698 (3), 0.191 (5) and 0.111 (5) for N20, N30 and N40, respectively]. Only the high-occupancy positions of Et_3NH^+ [N20 in (I) and (II)] are discussed. In the refinement procedure for (I) and (II), some geometrical parameters of the positions of the disordered cations (equivalent bond distances and angles but not torsion angles) were restrained to be equal. The positions of pairs of atoms in (II) (N30/N40, C31/C41, C32/C42, C33/C43 and C34/C44) were refined with the same *x*, *y*, *z* and anisotropic displacement parameters. All the non-H atoms were refined anisotropically, except for the low-occupancy positions of disordered atoms of the Et_3NH^+ cations in both (I) and (II). The H atoms of the anions in (I) and (II) and of the water molecule in (II) were found in difference Fourier maps and were refined isotropically, except for atoms H1′, H2′ and H2*W* in (II), which were refined with U_{iso}(H) values of U_{eq}(C1′,C2′) or $1.2U_{eq}$(O*W*). All H atoms of the disordered cations in (I) and (II) were positioned geometrically and treated as riding atoms, with N—H distances of 0.93 Å and C—H distances of 0.98 (methyl) or 0.99 Å (methylene), and with U_{iso}(H) values of $1.2U_{eq}$(N,C) or $1.5U_{eq}$(C).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3019). Services for accessing these data are described at the back of the journal.

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