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A new amine phosphate templated by tris(2-aminoethyl)amine

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The title compound, tris(2-ammonioethyl)amine dihydrogenphosphate monohydrogenphosphate, $C_6H_{21}N_4^{3+}\cdot HPO_4^{2-}\cdot H_2PO_4^{-}$, was prepared hydrothermally at 413 K over a period of 15 d. The structure exhibits extended polyanions, $[(HPO_4)(H_2PO_4)]_n^{3n-}$, constructed as O—H···O hydrogen-bonded ribbons. The triprotonated amine cations connect adjacent ribbons *via* N—H···O hydrogen bonds, giving rise to molecular sheets parallel to (010).

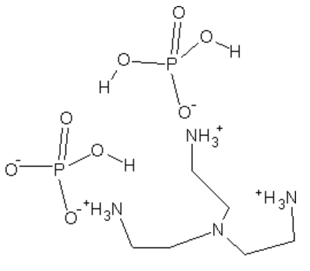
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.103
Data-to-parameter ratio = 17.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The synthesis of hybrid phosphates is of continuing interest because of their potential application in various fields (catalysis, fuel cells, protonic conductors, non-linear optics, *etc*.). Thus, numerous hydrogen phosphates with organic cations have been characterized, but to our knowledge, only three compounds with HPO_4^{2-} and $H_2PO_4^{-}$ entities together have been reported: $3C_{10}H_{16}NO^+\cdot H_2PO_4^-\cdot HPO_4^{2-}\cdot H_2O$ (Mukhopadhyay *et al*., 1989), $C_{12}H_{32}N_3^{3+}\cdot H_2PO_4^-\cdot HPO_4^{2-}\cdot 6H_2O$ (Neeraj & Natarajan, 2001) and $6C_3H_7N_6^+\cdot 4H_2PO_4^-\cdot HPO_4^{2-}\cdot H_2O$ (Janczak & Perpetuo, 2002). This paper describes the synthesis and crystal structure determination of a new organic hydrogen and dihydrogen monophosphate $C_6H_{21}N_4^{3+}\cdot HPO_4^{2-}\cdot H_2PO_4^-$, (I). Two crystallographically independent phosphate groups and a single triprotonated amine cation are present in the asymmetric unit of (I) (Fig. 1). The $HP2O_4^{2-}$ anions are assembled in dimers through strong [O7···O5^{ii} = 2.584 (2) Å; symmetry code: (ii) 1 $-x$, 1-y, 1-z] hydrogen bonds. Each dimer aggregates with four $H_2P1O_4^-$ groups *via* hydrogen bonding [O3···O8 = 2.526 (2) Å and O4···O6^{i} = 2.558 (2) Å; symmetry code: (i) 1 + x, y, z], forming extended inorganic ribbons, $[(HPO_4)(H_2PO_4)]_n^{3n-}$, parallel to the a axis (Fig. 2). These ribbons can be considered as polyanions, since the O···O distances in the hydrogen-bond scheme maintaining their cohesion is of the same order of magnitude as in the (PO_4) tetrahedron.



(I)

The triprotonated amine cations link adjacent polyanions *via* relatively weak hydrogen bonding (Table 2), forming molecular layers parallel to the (010) plane (Fig. 3). The

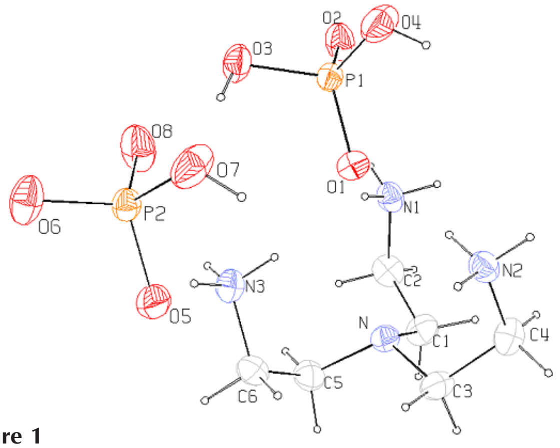


Figure 1
ORTEP view (Farrugia, 1997) of the asymmetric unit of (I). Displacement ellipsoids are shown at the 50% probability level.

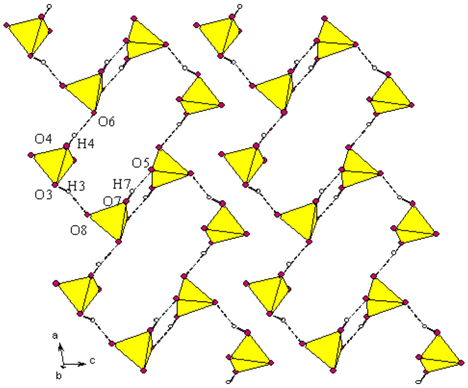


Figure 2
Extended $[(HPO_4)(H_2PO_4)]_n^{3n-}$ ribbons in (I). Dashed lines indicate hydrogen bonds.

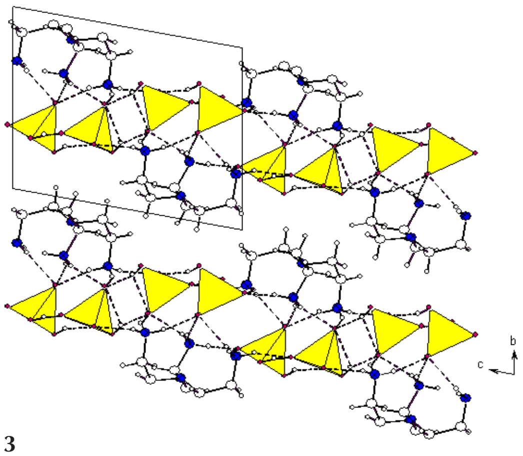


Figure 3
Projection of (I) along the *a* axis, showing the hydrogen-bonding interactions (dashed lines) between organic cations and the polyanions.

geometrical features of the two distinct phosphorus groups are quite regular (Table 1). For P2, d_{av} = 1.538 Å for P—O, with the longest distance [P2—O7 = 1.5826 (16) Å] corresponding to the protonated atom O7 and with θ_{av} = 109.44° for O—P—O. For P1, d_{av} = 1.541 Å for P—O, with the longest distances [P1—O3 = 1.5729 (15) Å and P1—O4 = 1.5671 (16) Å] corresponding to the P—O(H) bonds and with θ_{av} = 109.38° for O—P—O. The N—C and C—C distances and the C—N—C and C—C—N angles observed in the triprotonated amine cations lie within the ranges 1.474 (2)–1.516 (3) Å and 109.57 (15)–113.20 (16)°, respectively.

Experimental

The title compound was prepared from a starting mixture of Co(acetate)·2H_2O–H_3PO_4 (85%)–tris(2-aminoethyl)amine–ethanol in a 1:3.5:2.5:80 molar ratio under mild hydrothermal conditions (413 K, 15 d, autogenous pressure) in a Teflon-lined autoclave. The resulting product was washed with ethanol and dried in air. A suitable colorless single crystal of (I) was selected under a polarizing microscope.

Crystal data

$C_6H_{21}N_4^{3+}\cdot HO_4P^{2-}\cdot H_2O_4P^-$
M_r = 342.23
Triclinic, $P\overline{1}$
a = 7.905 (2) Å
b = 9.441 (2) Å
c = 10.974 (3) Å
α = 76.37 (2)°
β = 101.29 (3)°
γ = 105.96 (3)°
V = 757.7 (3) Å^3

Z = 2
D_x = 1.500 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 5.3–7.5°
μ = 0.33 mm^{-1}
T = 293 (2) K
Parallelepiped, colorless
0.26 × 0.19 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω/2θ scans
Absorption correction: none
3534 measured reflections
3290 independent reflections
2774 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

θ_{max} = 27.0°
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -14 \rightarrow 13$
2 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.103$
S = 1.05
3290 reflections
186 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.417P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.014 (3)

Table 1
Selected geometric parameters (Å, °).

P1—O2	1.5116 (15)	N—C3	1.478 (2)
P1—O1	1.5118 (14)	N—C1	1.480 (2)
P1—O4	1.5671 (16)	N1—C2	1.484 (3)
P1—O3	1.5729 (15)	N2—C4	1.477 (3)
P2—O8	1.5117 (15)	N3—C6	1.482 (2)
P2—O6	1.5231 (15)	C1—C2	1.516 (3)
P2—O5	1.5354 (15)	C3—C4	1.518 (3)
P2—O7	1.5826 (16)	C5—C6	1.516 (3)
N—C5	1.475 (3)		
O2—P1—O1	113.86 (9)	O5—P2—O7	108.37 (8)
O2—P1—O4	109.98 (10)	C5—N—C3	111.24 (15)
O1—P1—O4	111.09 (9)	C5—N—C1	109.90 (15)
O2—P1—O3	105.03 (8)	C3—N—C1	109.57 (15)
O1—P1—O3	111.70 (9)	N—C1—C2	112.86 (16)
O4—P1—O3	104.63 (9)	N1—C2—C1	112.14 (16)
O8—P2—O6	111.98 (9)	N—C3—C4	112.37 (16)
O8—P2—O5	110.52 (10)	N2—C4—C3	112.38 (16)
O6—P2—O5	110.84 (9)	N—C5—C6	113.20 (16)
O8—P2—O7	109.20 (10)	N3—C6—C5	112.56 (16)
O6—P2—O7	105.76 (9)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O8	0.82	1.77	2.526 (2)	152
N1—H1*C*···O1	0.89	2.16	2.968 (2)	151
N2—H2*C*···O1	0.89	2.01	2.859 (2)	160
N3—H3*A*···O5	0.89	2.08	2.905 (2)	153
N3—H3*A*···O8	0.89	2.54	3.161 (3)	127
N3—H3*C*···O1	0.89	2.00	2.846 (2)	158
O4—H4···O6^{i}	0.82	1.77	2.558 (2)	161
O7—H7···O5^{ii}	0.82	1.79	2.584 (2)	162
N1—H1*A*···O8^{iii}	0.89	1.97	2.760 (2)	147
N1—H1*B*···O2^{iv}	0.89	1.93	2.715 (2)	146
N2—H2*A*···O5^{i}	0.89	2.00	2.804 (2)	149
N3—H3*B*···O2^{iii}	0.89	1.97	2.733 (2)	142
N3—H3*B*···O3^{iii}	0.89	2.60	3.417 (2)	154

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

All H atoms were allowed to ride on their parent atoms, with O—H distances of 0.82 Å, N—H distances of 0.89 Å and C—H distances of 0.97 Å, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O,N). A common isotropic displacement parameter for C-bound H atoms refined to 0.0416 (19) Å^2.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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