

Triethanolammonium dihydrogenphosphate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

H-atom completeness 96%

Disorder in solvent or counterion

R factor = 0.037

wR factor = 0.084

Data-to-parameter ratio = 16.6

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

The structure of the title compound, $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+\cdot\text{H}_2\text{PO}_4^-$ or $\text{C}_6\text{H}_{16}\text{NO}_3^+\cdot\text{H}_2\text{PO}_4^-$, contains two distinct dihydrogenphosphate anions and two triethanolammonium cations in the asymmetric unit. The H_2PO_4 units are linked in a polymeric chain by strong $\text{P}-\text{OH}\cdots\text{O}-\text{P}$ hydrogen bonds along the [010] direction, while the $(\text{H}_2\text{PO}_4)^-$ and $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ ions are connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to yield sheet-like entities. The triethanolammonium cation shows a tripodal conformation and the ammonium H atom forms an intramolecular trifurcated hydrogen bond with the O atoms of the three ethanol groups.

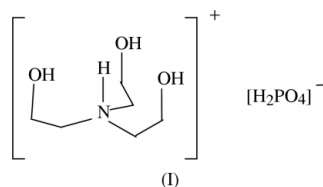
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Comment

Open-framework metal phosphates are generally synthesized under hydrothermal conditions in the presence of an amine. The main role of the amine is to behave as a structure-directing agent and also a ligand to the metal. Simple amine phosphates formed in the preparation of metal phosphates act as intermediates and sometimes occur as unexpected stable side products (Oliver *et al.*, 1998; Neeraj *et al.*, 1999). In the present study, we report the structure of triethanolammonium dihydrogenphosphate, (I).



The structure of (I) is composed of two distinct dihydrogenphosphate anions and two triethanolammonium cations in the asymmetric unit (Fig. 1). The N2-centred triethanolammonium cation is partially disordered over two positions [major component atoms C7, C9 and C11 with occupancy = 0.729 (4) and $d_{\text{av}}(\text{N}-\text{C}) = 1.501$ (3) \AA ; minor component atoms C7A, C9A and C11A with occupancy = 0.271 (4) and $d_{\text{av}}(\text{N}-\text{C}) = 1.495$ (9) \AA]. The triethanolammonium cation exhibits a tripodal conformation, in which the ammonium H atom forms an intramolecular trifurcated hydrogen bond with the O atoms of the three ethanol groups. Similar trifurcated intramolecular hydrogen bonds were observed in triethanolammonium bromide (Yilmaz *et al.*, 1996). The bonding geometry within the cation is comparable to those of other triethanolammonium salts with bromide (Yilmaz *et al.*, 1996), hexachloroplatinate (Yilmaz *et al.*, 1997), chloride and hydrogensulfide (Mootz *et al.*, 1990).

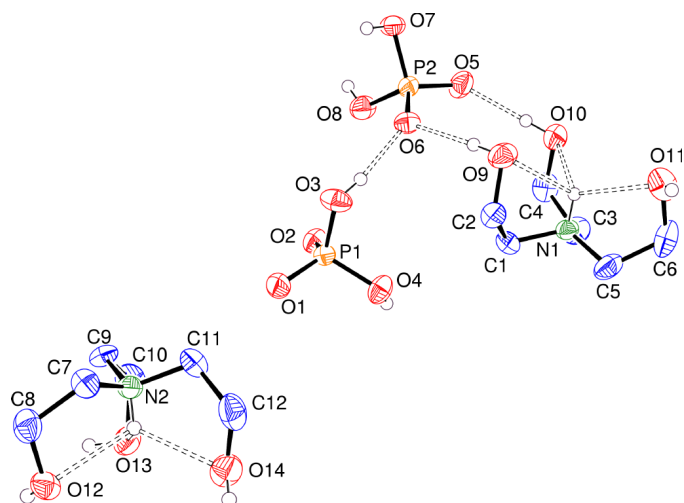


Figure 1
View of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii and H bonds are indicated by dashed lines. Only the major orientation (atoms C7, C9 and C11) of the N2-centred molecule is shown; all C–H H atoms have been omitted for clarity.

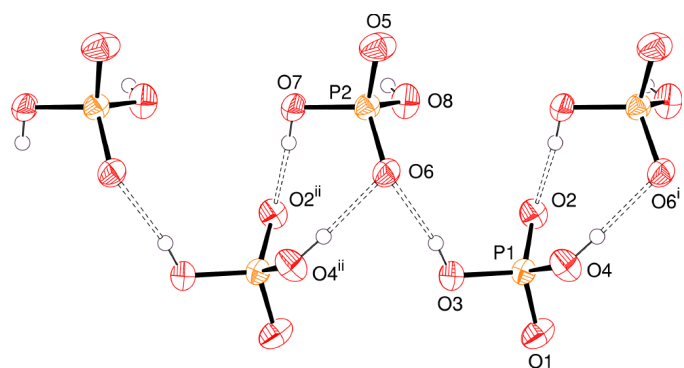


Figure 2
Details of the dihydrogen phosphate chain in (I), with hydrogen bonds indicated by dashed lines. Note how the P1 and P2 moieties are linked by alternating double and single hydrogen bonds. The symmetry codes are as in Table 2.

The crystal structure contains an extensive network of O–H···O hydrogen bonds. The H_2PO_4 units are linked in a polymeric chain by triple hydrogen bonds involving the OH and P=O groups along the [010] direction (Fig. 2). The $(\text{H}_2\text{PO}_4)^-$ and $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ ions are also connected by O–H···O hydrogen bonds to yield sheet-like entities (Fig. 3). Within the sheet the H_2PO_4 anions are hydrogen bonded in pairs and bridged by O–H_T···O_P (*T* = triethanolammonium, *P* = phosphate) type hydrogen bonds involving the ammonium ions. There is no hydrogen bonding between the neighbouring sheets, which are held together by van der Waals interactions.

Experimental

1.153 ml H_3PO_4 (17 mmol) (aqueous 85% wt) was added dropwise to a solution of triethanolamine (1.33 ml, 10 mmol) in 20 ml methanol and stirred for 30 min at room temperature. The resulting solution

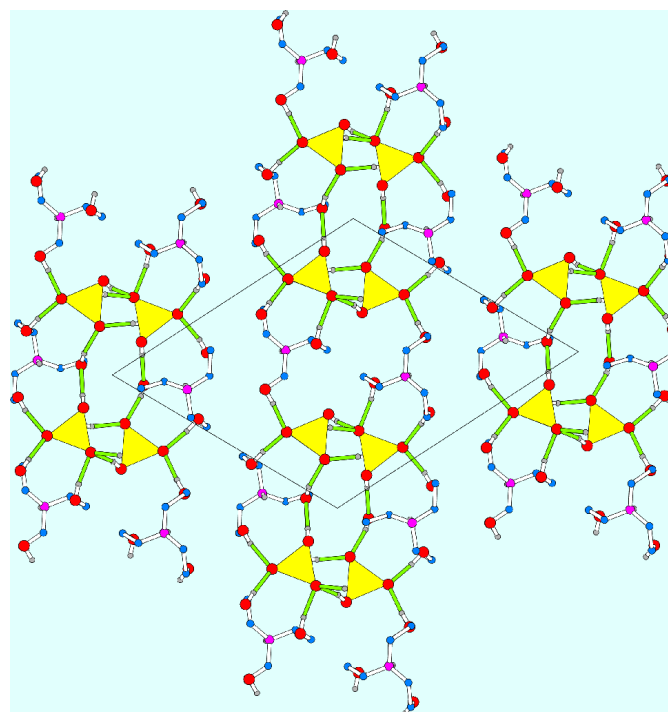


Figure 3
[010] projection of (I), showing the sheet-like arrangement of $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ and $(\text{H}_2\text{PO}_4)^-$ groups. Colour key: $[\text{H}_2\text{PO}_4]^-$ tetrahedra yellow, O atoms red, C atoms blue, N atoms purple, H atoms grey. The H···O portions of the hydrogen bonds are highlighted in green. C–H H atoms have been omitted for clarity.

was kept at 343 K for a day. X-ray quality crystals were formed when the solution was cooled to room temperature. Colourless transparent crystals of the title compound were washed with methanol and dried in air.

Crystal data

$\text{C}_6\text{H}_{16}\text{NO}_3^+ \cdot \text{H}_2\text{PO}_4^-$
 $M_r = 247.18$
Monoclinic, $P2_1$
 $a = 14.1354$ (7) Å
 $b = 5.5364$ (3) Å
 $c = 15.5323$ (7) Å
 $\beta = 116.354$ (1)°
 $V = 1089.21$ (9) Å³
 $Z = 4$

$D_x = 1.507$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 3525 reflections
 $\theta = 2.6$ – 28.1 °
 $\mu = 0.27$ mm⁻¹
 $T = 293$ (2) K
Blade, colourless
 $0.45 \times 0.12 \times 0.04$ mm

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.885$, $T_{\max} = 0.989$
9297 measured reflections

4714 independent reflections
3779 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 30.1$ °
 $h = -19 \rightarrow 19$
 $k = -5 \rightarrow 7$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.084$
 $S = 0.98$
4714 reflections
284 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
Absolute structure: Flack (1983),
2885 Friedel pairs
Flack parameter = 0.18 (8)

Table 1
Selected geometric parameters (Å).

P1—O1	1.4907 (17)	C3—C4	1.506 (4)
P1—O2	1.5034 (16)	C4—O10	1.414 (4)
P1—O3	1.567 (2)	C5—C6	1.507 (4)
P1—O4	1.5787 (17)	C6—O11	1.399 (4)
P2—O5	1.4915 (16)	N2—C7	1.484 (3)
P2—O6	1.5129 (15)	N2—C11	1.491 (3)
P2—O8	1.5688 (18)	N2—C9	1.527 (3)
P2—O7	1.5740 (17)	C7—C8	1.493 (4)
N1—C3	1.492 (3)	C8—O12	1.425 (4)
N1—C1	1.505 (3)	C9—C10	1.443 (4)
N1—C5	1.506 (3)	C10—O13	1.398 (4)
C1—C2	1.496 (4)	C11—C12	1.530 (4)
C2—O9	1.412 (3)	C12—O14	1.418 (4)

Table 2
Hydrogen-bonding 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>
O3—H1···O6	0.82	1.85	2.670 (2)	170
O4—H2···O6 ⁱ	0.88	1.82	2.680 (2)	166
O7—H3···O2 ⁱⁱ	0.81	1.84	2.642 (2)	171
O8—H4···O12 ⁱⁱⁱ	0.78	1.90	2.681 (2)	180
N1—H5···O9	0.91	2.33	2.818 (3)	113
N1—H5···O10	0.91	2.35	2.774 (3)	108
N1—H5···O11	0.91	2.35	2.830 (3)	113
O9—H18···O6	0.89	1.85	2.738 (2)	170
O10—H19···O5	0.84	1.85	2.690 (2)	178
O11—H20···O1 ^{iv}	0.89	1.79	2.671 (2)	175
N2—H21···O14	0.91	2.25	2.754 (3)	114
N2—H21···O12	0.91	2.32	2.768 (2)	110
N2—H21···O13	0.91	2.32	2.779 (3)	111
O12—H34···O2 ^v	0.80	1.88	2.655 (2)	163
O13—H35···O1 ^v	0.93	1.71	2.644 (2)	173
O14—H36···O5 ^{vi}	0.86	1.85	2.698 (2)	169

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

Water, hydroxyl and amine H atoms were found in difference maps and were refined, riding in their as-found positions. H atoms bonded to C atoms were placed in calculated positions 0.97 Å from their parent atoms and modelled by riding.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

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References

- Bruker (1999). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.02A) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. App. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Mootz, D., Brodalla, D. & Wiebcke, M. (1990). *Acta Cryst.* **C46**, 797–799.
- Neeraj, S., Natarajan, S. & Rao, C. N. R. (1999). *Angew. Chem. Int. Ed.* **38**, 3480–3483.
- Oliver, S., Lough, A. J. & Ozin, G. A. (1998). *Inorg. Chem.* **37**, 5021–5028.
- Shape Software (1999). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Yilmaz, V. T., Icbudak, H. & Howie, R. A. (1997). *Acta Cryst.* **C53**, 294–298.
- Yilmaz, V. T., Icbudak, H., Olmez, H. & Howie, R. A. (1996). *Turk. J. Chem.* **20**, 69–73.