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Crystal structure of tris(hydroxylammonium) orthophosphate

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The crystal structure of the title salt, $([H_3NOH]^+)_3\cdot[PO_4]^{3-}$, consists of discrete hydroxylammonium cations and orthophosphate anions. The atoms of the cation occupy general positions, whereas the anion is located on a threefold rotation axis that runs through the phosphorus atom and one of the phosphate O atoms. In the crystal structure, cations and anions are linked by intermolecular O—H···O and N—H···O hydrogen bonds into a three-dimensional network. Altogether, one very strong O—H···O, two N—H···O hydrogen bonds of medium strength and two weaker bifurcated N—H···O interactions are observed.

Keywords: crystal structure; hydroxylammonium salt; hydrogen bonding.

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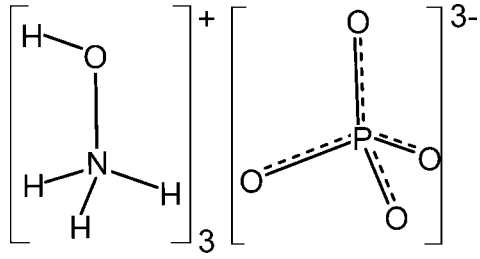
1. Related literature

The structure determination of the title compound was undertaken as a part of a project on the synthesis and structural characterization of hydroxylammonium salts with simple inorganic anions. For crystal structures of other hydroxylammonium salts with perchlorate, chloride or sulfate anions, see: Dickens (1969); Jerslev (1948); Shi *et al.* (1987); Mirceva & Golic (1995).



2. Experimental

2.1. Crystal data

$3H_4NO^+\cdot PO_4^{3-}$
M_r = 197.10
Trigonal, $R3c$: H
a = 10.7072 (9) Å
c = 11.0283 (13) Å
V = 1094.9 (2) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 170 K
0.15 × 0.12 × 0.11 mm

2.2. Data collection

Stoe IPDS-2 diffractometer
5420 measured reflections
647 independent reflections
621 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.090
S = 1.09
647 reflections
36 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Absolute structure: Flack x determined using 287 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.06 (9)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O3^{i}	0.84	1.70	2.540 (3)	172
N1—H1N1···O2^{ii}	0.91	1.90	2.785 (3)	163
N1—H2N1···O1^{iii}	0.91	2.37	3.110 (4)	138
N1—H2N1···O3^{iv}	0.91	2.20	2.884 (3)	132
N1—H3N1···O3	0.91	1.84	2.732 (3)	164

Symmetry codes: (i) $-y+\frac{4}{3}, x-y+\frac{2}{3}, z-\frac{1}{3}$; (ii) $-y+\frac{4}{3}, -x+\frac{2}{3}, z+\frac{1}{6}$; (iii) $x-\frac{1}{3}, x-y+\frac{1}{3}, z-\frac{1}{6}$; (iv) $-x+y+\frac{1}{3}, -x+\frac{2}{3}, z-\frac{1}{3}$.

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5223).

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supporting information

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Crystal structure of tris(hydroxylammonium) orthophosphate

Malte Leinemann, Inke Jess, Jan Boeckmann and Christian Näther

S1. Synthesis and crystallization

The title compound tris(hydroxylammonium) orthophosphate was synthesized by the reaction of 29.4 g H_3PO_4 (0.30 mol) with 29.7 g NH_2OH (0.90 mol) in aqueous solution under cooling. The resulting precipitate was filtered off, washed with mother liquor and dried in vacuum at 343 K for one day. The purity was checked by X-ray powder diffraction. Single crystals suitable for X-ray diffraction analysis were obtained by dissolving 0.5 g of the polycrystalline powder of tris-(hydroxylammonium)phosphate in 5 ml of water in a snap cap vial, allowing the solvent to evaporate slowly. After a few days colorless block-shaped crystals of the title compound were obtained.

S2. Refinement

The N–H and O–H hydrogen atoms were located in a difference map but in the final refinement they were positioned with idealized geometry allowed to rotate but not to tip. H atoms were refined with U_{iso}(H) = 1.5U_{eq}(N,O) using a riding model with O—H = 0.82 Å and N—H = 0.99 Å, respectively.

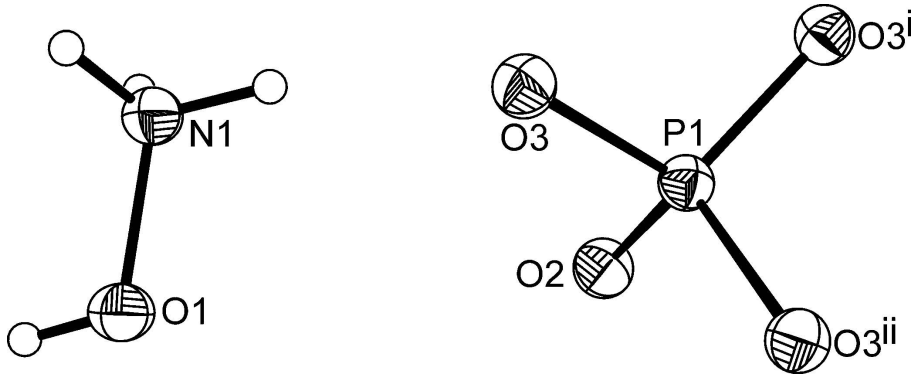

Figure 1

View of the molecular components of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: i) = -x+y, -x+1, z, ii) = -y+1, x-y, z.]

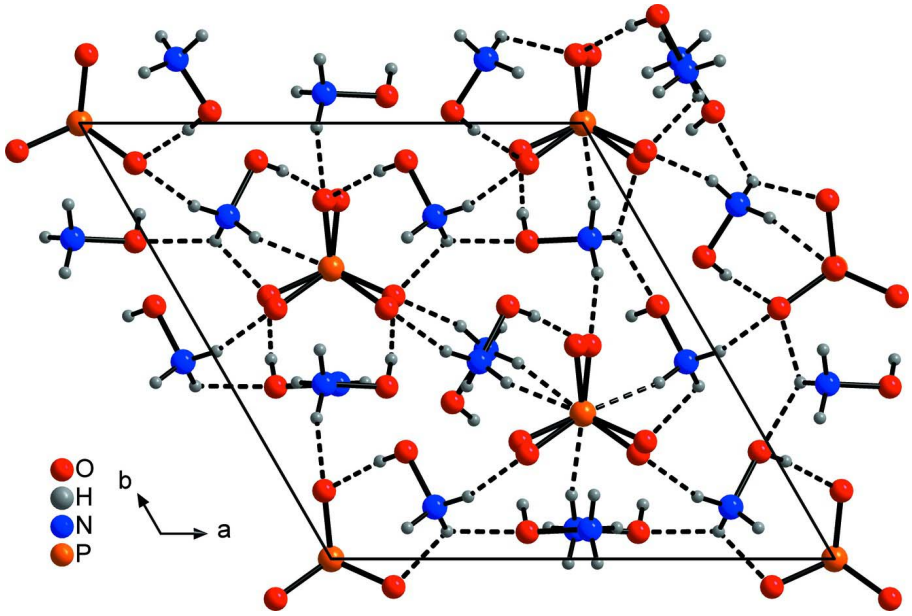

Figure 2

Crystal structure of the title compound in a view along the crystallographic *c* axis. Intermolecular hydrogen bonding is shown as dashed lines. For clarity, only parts of the hydrogen bonding interactions are shown.

Tris(hydroxylammonium) orthophosphate

Crystal data

$3H_4NO^+·PO_4^{3-}$
M_r = 197.10
Trigonal, *R*3*c*:*H*
a = 10.7072 (9) Å
c = 11.0283 (13) Å
V = 1094.9 (2) Å^3
Z = 6
F(000) = 624
D_x = 1.793 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5420 reflections
θ = 7.6–59.2°
μ = 0.39 mm^{-1}
T = 170 K
Block, colorless
0.15 × 0.12 × 0.11 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
5420 measured reflections
647 independent reflections
621 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 29.0°, θ_{min} = 3.8°
h = −14→14
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.090
S = 1.09
647 reflections
36 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.3897P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Absolute structure: Flack x determined using 287 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.06 (9)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.6408 (2)	0.5792 (2)	0.5089 (3)	0.0230 (5)
H1O1	0.6827	0.5567	0.4562	0.035*
N1	0.5202 (3)	0.4522 (2)	0.5550 (2)	0.0203 (5)
H1N1	0.5515	0.4032	0.6016	0.030*
H2N1	0.4668	0.3955	0.4922	0.030*
H3N1	0.4649	0.4767	0.6008	0.030*
P1	0.3333	0.6667	0.64509 (11)	0.0166 (3)
O2	0.3333	0.6667	0.5059 (3)	0.0223 (8)
O3	0.3977 (2)	0.5747 (2)	0.69256 (18)	0.0202 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0240 (11)	0.0183 (9)	0.0246 (9)	0.0089 (8)	0.0057 (9)	0.0017 (8)
N1	0.0201 (11)	0.0179 (12)	0.0219 (12)	0.0087 (10)	0.0025 (10)	0.0006 (10)
P1	0.0171 (3)	0.0171 (3)	0.0157 (5)	0.00855 (17)	0.000	0.000
O2	0.0233 (11)	0.0233 (11)	0.0205 (18)	0.0116 (6)	0.000	0.000
O3	0.0207 (10)	0.0200 (9)	0.0200 (10)	0.0103 (8)	−0.0003 (9)	−0.0002 (8)

Geometric parameters (Å, º)

O1—N1	1.421 (3)	P1—O2	1.535 (4)
O1—H1O1	0.8400	P1—O3^{i}	1.548 (2)
N1—H1N1	0.9100	P1—O3^{ii}	1.548 (2)
N1—H2N1	0.9100	P1—O3	1.548 (2)
N1—H3N1	0.9100		
N1—O1—H1O1	109.5	O2—P1—O3^{i}	109.77 (9)
O1—N1—H1N1	109.5	O2—P1—O3^{ii}	109.77 (9)
O1—N1—H2N1	109.5	O3^{i}—P1—O3^{ii}	109.17 (9)
H1N1—N1—H2N1	109.5	O2—P1—O3	109.77 (9)
O1—N1—H3N1	109.5	O3^{i}—P1—O3	109.17 (9)
H1N1—N1—H3N1	109.5	O3^{ii}—P1—O3	109.17 (9)
H2N1—N1—H3N1	109.5		

Symmetry codes: (i) −*y*+1, *x*−*y*+1, *z*; (ii) −*x*+*y*, −*x*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···O3^{iii}	0.84	1.70	2.540 (3)	172
N1—H1*N*1···O2^{iv}	0.91	1.90	2.785 (3)	163
N1—H2*N*1···O1^{v}	0.91	2.37	3.110 (4)	138
N1—H2*N*1···O3^{vi}	0.91	2.20	2.884 (3)	132
N1—H3*N*1···O3	0.91	1.84	2.732 (3)	164

Symmetry codes: (iii) −*y*+4/3, *x*−*y*+2/3, *z*−1/3; (iv) −*y*+4/3, −*x*+2/3, *z*+1/6; (v) *x*−1/3, *x*−*y*+1/3, *z*−1/6; (vi) −*x*+*y*+1/3, −*x*+2/3, *z*−1/3.