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Tris(5-amino-1*H*-1,2,4-triazol-4-ium) dihydrogenphosphate hydrogenphosphate trihydrate

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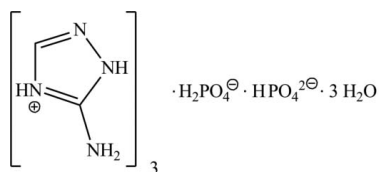
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{N}-\text{C}) = 0.002$ Å; R factor = 0.023; wR factor = 0.059; data-to-parameter ratio = 19.3.

In the crystal structure of the title molecular salt, $3\text{C}_2\text{H}_5\text{N}_4^{+} \cdot \text{HPO}_4^{2-} \cdot \text{H}_2\text{PO}_4^{-} \cdot 3\text{H}_2\text{O}$, the phosphate-based framework is built upon layers parallel to (010) made up from the $\text{H}_2\text{PO}_4^{-}$ and HPO_4^{2-} anions and water molecules, which are interconnected through $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. The organic cations are located between the phosphate-water layers and are connected to them *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The bond-length features are consistent with an imino resonance form for the exocyclic amino group, as is commonly found for a $\text{C}-\text{N}$ single bond involving sp^2 -hybridized C and N atoms.

Related literature

For applications of organic phosphate complexes, see: Bringley & Rajeswaran (2006); Dai *et al.* (2002); Masse *et al.* (1993). For graph-set motifs and theory, see: Bernstein *et al.* (1995). For reference structural data, see: Kaabi *et al.* (2004); Shanmuga Sundara Raj *et al.* (2000). For P—OH bond lengths, see: Chtioui & Jouini (2005).



Experimental

Crystal data

$3\text{C}_2\text{H}_5\text{N}_4^{+} \cdot \text{HO}_4\text{P}^{2-} \cdot \text{H}_2\text{O}_4\text{P}^{-} \cdot 3\text{H}_2\text{O}$ $V = 1003.5$ (2) Å³
 $M_r = 502.31$ $Z = 2$
 Monoclinic, Pc $\text{Mo K}\alpha$ radiation
 $a = 10.4793$ (13) Å $\mu = 0.30$ mm⁻¹
 $b = 8.7655$ (11) Å $T = 100$ K
 $c = 11.4536$ (14) Å $0.60 \times 0.35 \times 0.18$ mm
 $\beta = 107.489$ (2)°

Data collection

Bruker SMART APEX CCD 13833 measured reflections
 diffractometer 6229 independent reflections
 Absorption correction: multi-scan 6132 reflections with $I > 2\sigma(I)$
 (SADABS; Bruker, 2011) $R_{\text{int}} = 0.016$
 $T_{\text{min}} = 0.693$, $T_{\text{max}} = 0.746$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.059$ $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $S = 1.04$ $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³
 6229 reflections Absolute structure: Flack (1983), 2950 Friedel pairs
 322 parameters Flack parameter: -0.02 (4)
 32 restraints

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1A}-\text{H1A1} \cdots \text{O3B}$	0.85 (1)	2.31 (1)	3.1356 (13)	162 (2)
$\text{N1A}-\text{H1A2} \cdots \text{N3A}^{\text{i}}$	0.85 (1)	2.19 (1)	3.0305 (15)	170 (2)
$\text{N2A}-\text{H2A} \cdots \text{O4B}$	0.88	1.77	2.6130 (13)	161
$\text{N4A}-\text{H4A} \cdots \text{O4B}^{\text{j}}$	0.88	1.76	2.6314 (13)	171
$\text{N1B}-\text{H1B1} \cdots \text{O2}$	0.86 (1)	1.96 (1)	2.8214 (13)	178 (2)
$\text{N1B}-\text{H1B2} \cdots \text{N3B}^{\text{i}}$	0.82 (1)	2.28 (1)	3.0639 (15)	160 (2)
$\text{N2B}-\text{H2B1} \cdots \text{O3}^{\text{ii}}$	0.88	1.84	2.6824 (13)	159
$\text{N4B}-\text{H4B} \cdots \text{O1A}^{\text{iii}}$	0.88	1.87	2.7376 (12)	167
$\text{N1C}-\text{H1C1} \cdots \text{N3C}^{\text{i}}$	0.83 (1)	2.18 (1)	3.0028 (14)	172 (2)
$\text{N1C}-\text{H1C2} \cdots \text{O3A}$	0.86 (1)	2.24 (1)	3.0589 (13)	160 (2)
$\text{N2C}-\text{H2C} \cdots \text{O4A}$	0.88	1.78	2.6278 (12)	161
$\text{N4C}-\text{H4C} \cdots \text{O4A}^{\text{i}}$	0.88	1.79	2.6645 (12)	170
$\text{O2A}-\text{H2AB} \cdots \text{O3B}^{\text{iv}}$	0.76	1.95	2.6593 (11)	155
$\text{O1B}-\text{H1B} \cdots \text{O3A}$	0.77	1.80	2.5495 (12)	161
$\text{O2B}-\text{H2BA} \cdots \text{O1}^{\text{v}}$	0.83	1.73	2.5552 (12)	176
$\text{O1}-\text{H1D} \cdots \text{O2}$	0.84 (1)	1.93 (1)	2.7439 (12)	166 (2)
$\text{O1}-\text{H1E} \cdots \text{O3B}$	0.80 (1)	1.91 (1)	2.6968 (12)	168 (2)
$\text{O2}-\text{H2D} \cdots \text{O1A}^{\text{v}}$	0.82 (1)	1.90 (1)	2.7024 (11)	168 (2)
$\text{O2}-\text{H2E} \cdots \text{O3A}^{\text{iii}}$	0.81 (1)	1.95 (1)	2.7566 (12)	178 (2)
$\text{O3}-\text{H3D} \cdots \text{O2B}$	0.79 (1)	2.14 (2)	2.8515 (12)	149 (2)
$\text{O3}-\text{H3E} \cdots \text{O1A}^{\text{iii}}$	0.80 (1)	1.92 (1)	2.7085 (11)	176 (2)

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

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Hübschle *et al.*, 2011); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2044).

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Tris(5-amino-1*H*-1,2,4-triazol-4-ium) dihydrogenphosphate hydrogenphosphate trihydrate

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S1. Comment

Inorganic–organic hybrid compounds provide a class of materials with interesting technological applications (Bringley & Rajeswaran, 2006; Dai *et al.*, 2002). Among these materials, compounds with noncentrosymmetric crystallographic structures are interesting for their applications in quadratic non-linear optical materials research (Masse *et al.*, 1993). Their abilities to combine the rigidity and high cohesion of inorganic host matrices with the enhanced polarizability of organic guest chromophores within one molecular scale assists in better performance of optical signal-processing devices. The use of organic-inorganic polar crystalline materials for quadratic nonlinear optical applications is supported by two observations:

(i) the organic molecules, especially if they contain a delocalized π -system with asymmetric substitution by electron donor-acceptor groups, are highly polarizable entities ideally suited for NLO applications. Being organic materials, the nature of the substituents can be tailored so as to not affect optical transparency;

(ii) the ionic inorganic host matrices are able to increase the packing cohesion, can induce noncentrosymmetry, and also shift the transparency of crystal towards blue wavelengths.

Within a systematic investigation of new materials resulting from the association of organic chromophores with inorganic species, we report here the synthesis and the characterization of a new hybrid phosphate-amine material, $(\text{C}_2\text{H}_5\text{N}_4)_3(\text{HPO}_4)(\text{H}_2\text{PO}_4)\cdot 3\text{H}_2\text{O}$, which includes the 3-amino-1*H*-1,2,4-triazolium cations, a chromophore which could be efficient in the blue-U.V. wavelength region. The title compound could exhibit a richness of interesting physical properties such as ferroelectricity and nonlinear optic phenomena like second harmonic generation. It crystallizes in a non-centrosymmetric setting in the space group *Pc*. The structure of this organic-inorganic hybrid material consists of one dihydrogenmonophosphate anion, one monohydrogenmonophosphate dianion, three crystallographically independent 3-amino-1*H*-1,2,4-triazolium cations and three water molecules (Fig. 1). The atomic arrangement is a typical layered organization as it is very often encountered in this kind of inorganic-organic hybrid compounds (Kaabi *et al.*, 2004). The H_2PO_4^- anions are hydrogen bonded with the HPO_4^{2-} groups and one of the water molecules (that of O3) to form corrugated chains running parallel to the *a*-axis at (0, 0, 0) and (0, 0, 1/2). These chains are interconnected, *via* O(water)—H \cdots O and O—H \cdots O(water) hydrogen bonds, with the two remaining water molecules $\text{H}_2\text{O}(1)$ and $\text{H}_2\text{O}(2)$, associated through O1—H \cdots O2 hydrogen bonds, on one hand, and with the HPO_4^{2-} anions of the adjacent chain, through O—H \cdots O hydrogen bonds, on the other hand. These hydrogen bonds link the different inorganic units into infinite planar layers parallel to the (0 1 0) plane (Fig. 2) crossing the unit cell at $y = (2n + 1)/2$ (Fig. 3). Within the layers, various graph-set motifs (Bernstein *et al.*, 1995) are apparent, including $R_5^5(10)$ and $R_4^4(12)$ loops. The 3-amino-1*H*-1,2,4-triazolium cations are interconnected *via* weak N—H \cdots N hydrogen bonds, with D—H \cdots A distances between 3.003 (1) and 3.064 (1)

Å, to form organic chains spreading along the *c*-axis at $x \sim (n + 1)/3$ (Fig. 4). The chains are build from the three crystallographically independent organic cations, labelled A, B and C, in such a way that each N—H \cdots N connected chain incorporates only one type of cation: Molecules of type A are located at $x \sim 1/3$, chains at $x \sim 0$ consist of molecules of type B, and the chains at $x \sim 2/3$ are made up of molecules C. Alternating molecules in each of these chains are created by the *c*-glide plane. In two of the chains, that of molecules A and C, alternating molecules are roughly coplanar. In the third, molecules are twisted against each other by an angle of 34.37°. The chains are roughly parallel to each other and weakly π -stacked, with interplanar distances between the mean planes of chains between 3.21 Å (between A and C), and up to 3.52 Å (for A and B). Despite of the quite close interplanar distances, π - π stacking interactions are limited due to molecule offsets in parallel layers, and the non-coplanarity of neighboring molecules in the chains of molecules B. The organic chains are anchored to the inorganic layers through N—H \cdots O hydrogen bonds whose geometrical characteristics are given in Table 2. The projection of the whole arrangement along the *a*-axis (Fig. 4) shows how the organic chains alternate as to fill the space separating parallel inorganic layers. In this structure, three 3-amino-1*H*-1,2,4-triazolium cationic groups compensate the negative charges of the dihydrogenmonophosphate and the mono-hydrogenmonophosphate anions, leading to charge neutrality for the structure as a whole.

The sum of the angles around the N1A, N1B and N1C nitrogen atoms are 360° and the C—N bond distances of the NH₂ groups are 1.332 (1) Å for N1A—C1A, 1.327 (1) Å for N1B—C1B and 1.330 (1) Å for N1C—C1C, which are short for C—N single bonds, but still not quite as contracted as one would expect for a fully established C=N double bond. These bond length features are consistent with an imino resonance form as it is commonly found for a C—N single bond involving *sp*² hybridized C and N atoms (Shanmuga Sundara Raj *et al.*, 2000). In agreement with this, the amino groups are not pyramidal but the electron densities of the hydrogen atoms of the amino groups were found to be in plane with the 3-amino-1*H*-1,2,4-triazolium skeleton. The detailed geometry of the HP(1 A)O₄²⁻ and H₂P(1B)O₄⁻ anions shows two kinds of P—O distances. The shortest ones, 1.5243 (8), 1.5294 (8) and 1.5364 Å for the first anion (labelled A) and 1.5132 (8) and 1.5163 (8) Å for the second one (labelled B), correspond to the phosphorous atom doubly bonded to the oxygen atom, while the largest ones 1.5845 (8) Å and (1.5612 (8), 1.5741 (8) Å, respectively, can be attributed to the P—OH bond length. This is in agreement with the literature data (Chtioui & Jouini, 2005). Refining the structure in the asymmetric space group gives a value of -0.02 (4) for the Flack parameter (Flack, 1983), confirming the absolute structure and absence of twinning.

S2. Experimental

Crystals of the title compound were prepared at room temperature by slow addition of a solution of orthophosphoric acid (8 mmol in 30 ml of water) to an alcoholic solution of 3-amino-1*H*-1,2,4-triazole (12 mmol in 30 ml of ethanol). The acid was added until the alcoholic solution became turbid. After filtration, the solution was allowed to slowly evaporate at room temperature over several days leading to formation of transparent prismatic crystals with suitable dimensions for single-crystal structural analysis (1.2 mg, 2.4 mmol, yield 60%). The crystals are stable for months under normal conditions of temperature and humidity.

S3. Refinement

H atoms were placed in calculated positions with the exception of water and NH₂ H atoms, which were located in difference density maps and were refined. C—H distances were set to 0.95 Å, N_{ring}—H distances to 0.88 Å. H atoms of P-bound hydroxy groups were placed geometrically with fixed P—O—H angles, but with variable torional angles and O—H distances to best fit the experimental electron density (AFIX 148 in *SHELXTL*, Sheldrick 2008). All H₂O O—H distances were restrained to be similar within a standard deviation of 0.02 Å. All amino N—H distances were also

restrained to be similar within the same standard deviation. U_{iso} values of H atoms were set to 1.2 or 1.5 times U_{eq} of their respective carrier atom for amino and O-bound H atoms respectively.

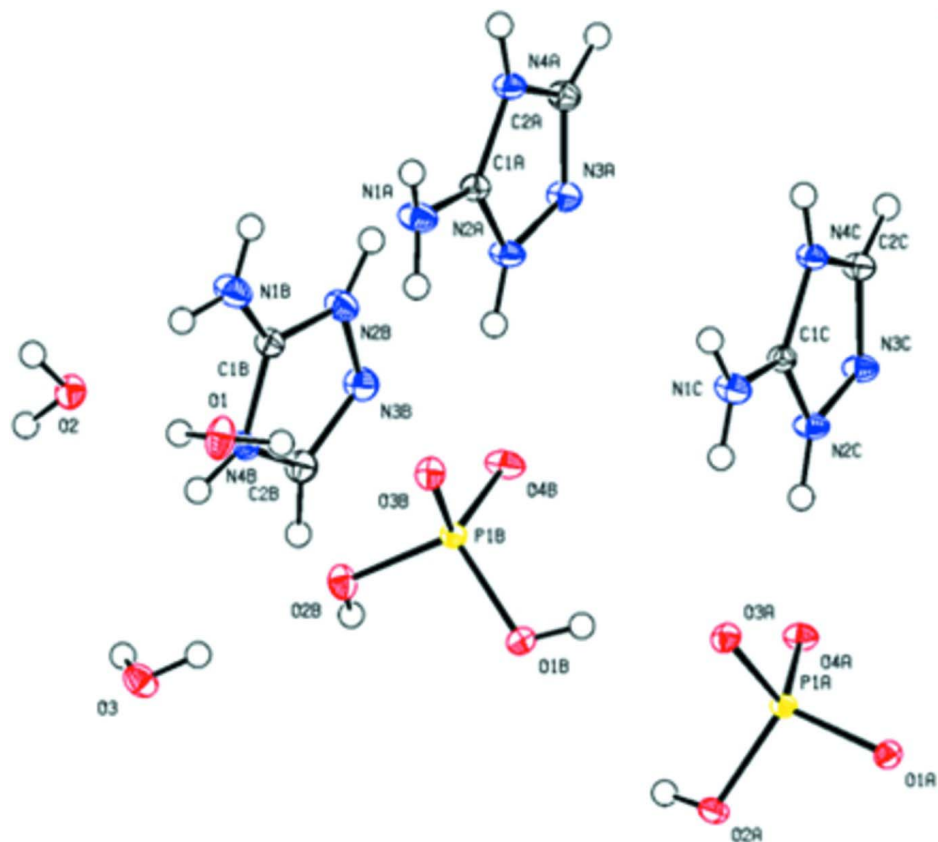


Figure 1

A view of the title compound, showing 40% probability displacement ellipsoids and arbitrary spheres for the H atoms.

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