Crystal structure of *o*-aminopyridinium dihydrogenmonophosphate, $(NH_2C_5H_4NH)[H_2PO_4]$

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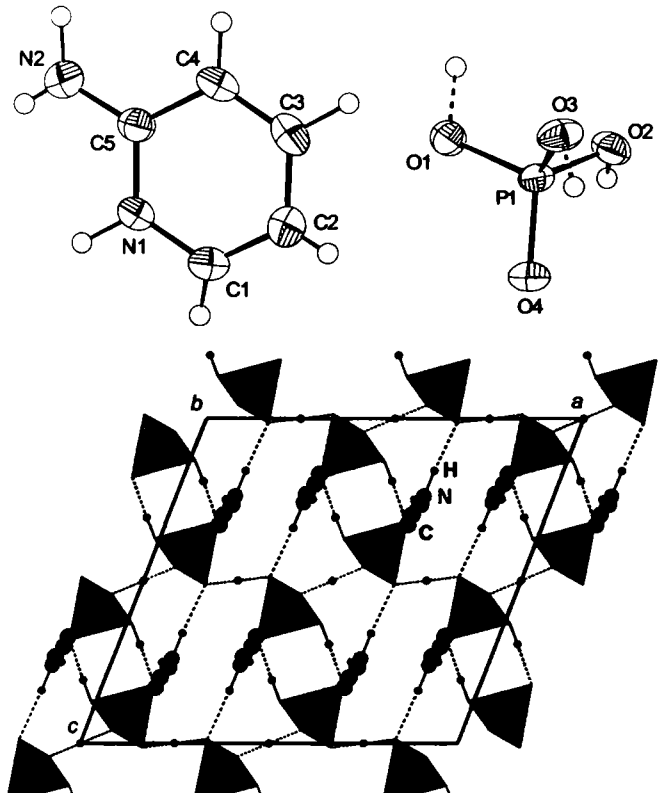

Abstract

$C_5H_9N_2O_4P$, monoclinic, *C*12/*c*1 (no. 15), $a = 13.462(4)$ Å, $b = 10.209(3)$ Å, $c = 12.582(4)$ Å, $\beta = 110.96(3)°$, $V = 1614.8$ Å^3, $Z = 8$, $R_{gt}(F) = 0.036$, $wR_{ref}(F) = 0.046$, $T = 296$ K.

Source of material

The hybrid compound was prepared by adding orthophosphoric acid to water, followed by the addition of 2-aminopyridine. The mixture was heated and stirred for two hours to attain homogeneity. The resulting solution was slowly evaporated at room temperature for several days, led to colorless single crystals, stable for long time under normal conditions of temperature and moisture.

Discussion

The asymmetric unit of the structure of $(2\text{-}NH_2C_5H_4NH)H_2PO_4$ consists of one phosphate anion and one organic cation (figure, top). The unit cell projection along the *b* axis (figure bottom) shows that the H_2PO_4 tetrahedra are connected by hydrogen bonds of O–H···O type, forming centrosymmetric units of the formula $[H_4P_2O_8]^{2-}$. The two hydrogen atoms H(O1) and H(O3) are located in the special positions ½,0,0 and ¾,¼,0 with half occupation. This has permitted to every unit to connect four of its neighbors through strong symmetrical hydrogen bonds of the O–H···O type (O1···O1′ = 2.470(2) Å and O3···O3′ = 2.466(2) Å), thus giving three-dimensional anionic network. Similar strong symmetrical hydrogen bonds are found in crystal structures of other phosphates, such as $CsMnHP_3O_{10}$ [1], $RbMnHP_3O_{10}$ [2] and $[OC_4H_8N(CH_3)CH_2COOH_3PO_4]$ [3]. The pyridine ring of the organic cation is planar, with a mean plane deviation of 0.0045(1) Å. The C5—N2 bond length of 1.323(2) Å is approximately equal to C=N double bond length, indicating that N2 atom of the amino group must be sp^2 hybridized. This is also supported by the C5–N2–H6 angle of 119.6°, and by the fact that atoms C5, N2, H5 and H6 lie almost in the pyridine plane. Main bond lengths and angles of these entities are as expected. The *o*-aminopyridinium cations are anchored onto the anionic three-dimensional network with similar direction, by forming hydrogen bonds with the oxygen atoms with N–H···O distances in the range 2.739(2) Å – 2.979(2) Å. These hydrogen bonds contribute to the stability of the network of the crystal structure. This latter is additionally stabilized by π-π interactions considered as weak intermolecular interactions, between organic molecules stacked in opposition to each other along the *a* axis ($d = 3.51$ Å).

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.40 × 0.50 × 1.10 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	1.71 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius Mach3, $\omega/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3151, 3036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 2066
$N(param)_{refined}$:	109
Programs:	SIR92 [4], teXsan [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*b*	½	0	0	0.028
H(2)	8*f*	0.4436	0.1756	–0.1945	0.028
H(3)	4*d*	¾	¼	0	0.028
H(4)	8*f*	0.9008	–0.3412	0.0925	0.028
H(5)	8*f*	0.8649	–0.4045	0.2494	0.028
H(6)	8*f*	0.8421	–0.3327	0.3381	0.028
H(7)	8*f*	0.8245	–0.0954	0.2985	0.049
H(8)	8*f*	0.8894	–0.1867	–0.0208	0.028
H(9)	8*f*	0.8533	0.0873	0.2001	0.028
H(10)	8*f*	0.8946	0.0289	0.0435	0.028

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	8*f*	0.59372(2)	0.12968(3)	−0.08668(2)	0.0296(1)	0.0277(1)	0.0225(1)	−0.0054(1)	0.01291(9)	−0.0028(1)
O(1)	8*f*	0.57060(7)	−0.00246(8)	−0.04119(8)	0.0468(5)	0.0252(4)	0.0485(5)	−0.0047(3)	0.0311(4)	−0.0011(3)
O(2)	8*f*	0.48690(7)	0.20950(9)	−0.12942(7)	0.0396(4)	0.0387(4)	0.0300(4)	0.0049(3)	0.0150(3)	−0.0063(3)
O(3)	8*f*	0.66830(7)	0.21009(9)	0.01220(7)	0.0427(5)	0.0424(5)	0.0258(4)	−0.0157(4)	0.0146(3)	−0.0091(3)
O(4)	8*f*	0.63563(6)	0.10749(9)	−0.18107(7)	0.0329(4)	0.0418(4)	0.0253(4)	−0.0005(3)	0.0147(3)	−0.0033(3)
N(1)	8*f*	0.87961(8)	−0.2587(1)	0.10794(9)	0.0399(5)	0.0320(5)	0.0322(5)	0.0048(4)	0.0175(4)	−0.0027(4)
N(2)	8*f*	0.8435(1)	−0.3448(1)	0.2601(1)	0.0629(8)	0.0389(6)	0.0396(6)	0.0029(5)	0.0262(6)	0.0028(4)
C(1)	8*f*	0.8915(1)	−0.1571(1)	0.0437(1)	0.0529(7)	0.0427(7)	0.0357(6)	0.0077(6)	0.0248(6)	0.0014(5)
C(2)	8*f*	0.8807(1)	−0.0321(1)	0.0727(1)	0.0667(9)	0.0363(6)	0.0556(9)	0.0074(6)	0.0357(8)	0.0090(6)
C(3)	8*f*	0.8567(1)	−0.0094(1)	0.1712(1)	0.0587(8)	0.0337(6)	0.0558(8)	0.0097(6)	0.0289(7)	−0.0042(6)
C(4)	8*f*	0.8428(1)	−0.1112(1)	0.2340(1)	0.0469(7)	0.0407(7)	0.0393(6)	0.0056(5)	0.0233(5)	−0.0073(5)
C(5)	8*f*	0.8551(1)	−0.2417(1)	0.2020(1)	0.0319(5)	0.0354(5)	0.0285(5)	0.0033(4)	0.0118(4)	−0.0014(4)

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