Z. Kristallogr. NCS 220 (2005) 147-148

Crystal structure of 2-ethyl-6-methylanilinium dihydrogenphosphate phosphoric acid, $(C_9H_{14}N)H_2PO_4 \cdot H_3PO_4$

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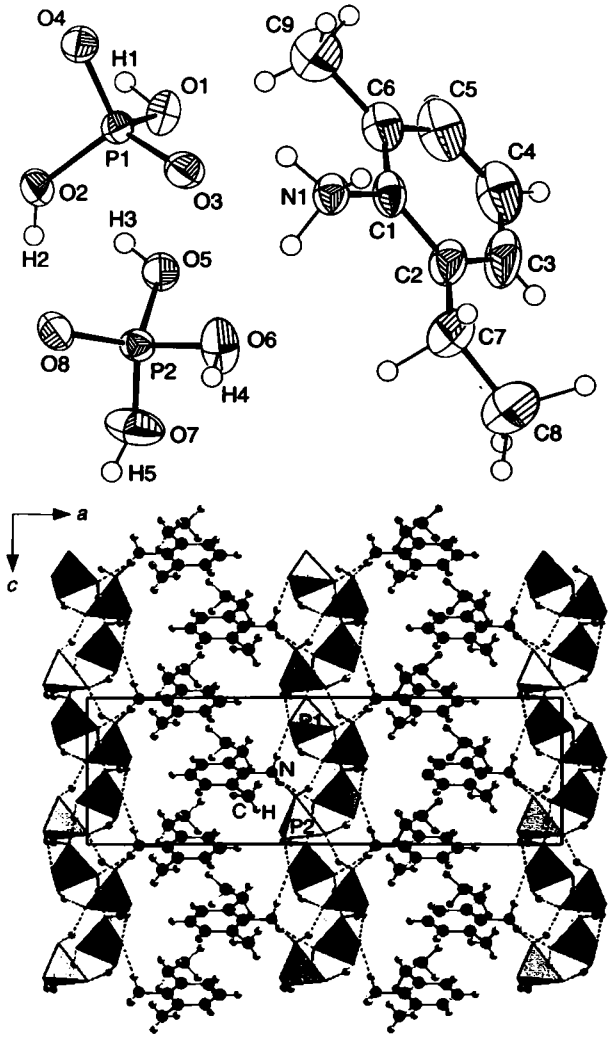
Received December 28, 2004, accepted and available on-line February 28, 2005; CCDC no. 1267/1453



Abstract

$C_9H_{19}NO_8P_2$, orthorhombic, $Pca2_1$ (no. 29), $a = 24.348(4)$ Å, $b = 8.088(2)$ Å, $c = 7.623(4)$ Å, $V = 1501.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.039$, $wR_{ref}(F) = 0.049$, $T = 296$ K.

Source of material

Crystals of title compound were synthesized by reaction of stirred ethanolic solution of 2-ethyl-6-methylaniline with concentrated phosphoric acid. Then, the obtained solution was evaporated in air for several days at room temperature until formation of prismatic crystals with suitable size for X-ray analysis.

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Discussion

The acentric space group $Pca2_1$ is confirmed by a positive (SHG) test on a powdered sample using an Nd^{3+}: YAG laser fundamental beam (1.06 μm). The asymmetric unit consists of three fundamentals entities, the H_3PO_4 molecule, the $H_2PO_4^-$ anion and the organic $C_9H_{14}N^+$ cation (figure, top). The crystal structure of the title compound is built by alternate inorganic and organic layers along the *a* axis and linked by strong N–H···O hydrogen bonds (figure, bottom). The $H_2PO_4^-$ anions and H_3PO_4 molecules are connected alternately by O–H···O hydrogen bonds to form infinite corrugated inorganic chains parallel to the *b,c* plane and centered at $x = 0$ and ½. The organic $C_9H_{14}N^+$ cations are organized in opposite direction along the *c* axis between the inorganic layers and situated at $x = ¼$ and ¾, so that each one establishes another kind of strong N–H···O hydrogen bonds with the anionic chains involving the three hydrogen atoms of the NH_3 group bonded to one phosphoric acid molecule and two $H_2PO_4^-$ anions. As a result, these two types of hydrogen bonds contribute to the cohesion in the network of the present crystal structure.

The comparison of this structure with that one of $HisH^+ \cdot H_2PO_4^- \cdot H_3PO_4$ [1] shows that both structures are built up by a large number of similar hydrogen bonds formed between *R*-NH_3 groups, dihydrogenphosphate anions and phosphoric acid molecules and present also infinite hydrogen-bonded layers. In spite of these similarities, the molecules of phosphoric acid are not hydrogen-bonded to each other in the latter structure [1], since the imidazolium cations also participate on the hydrogen bonding system. The structure of the title compound is also closely related to that of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]H_2PO_4$ [2]. In fact, these two structures have a similarly typical layered organization and the same arrangement in opposite direction of organic cations. Furthermore, the inorganic anion chains screen the interaction between the organic cations and probably lead to a non-centrosymmetric atomic arrangement in the two structures. Therefore, the title compound could be an interesting material in the non-linear optics. Its absolute structure could not be determined.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.30 × 0.45 × 0.70 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	1.73 cm^{-1}
Diffractometer, scan mode:	MACH3, $\omega/2\theta$
$2\theta_{max}$:	51.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3421, 3421
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 2338
$N(param)_{refined}$:	180
Programs:	SIR92 [3], teXsan [4]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.9743	0.5608	0.8183	0.053
H(2)	4*a*	1.0471	0.2560	0.8709	0.093
H(3)	4*a*	0.9162	0.2753	0.9795	0.072
H(4)	4*a*	0.9682	−0.0179	0.6185	0.049
H(5)	4*a*	0.9297	−0.1673	0.9869	0.064
H(6)	4*a*	0.9084	0.4134	0.5759	0.039
H(7)	4*a*	0.9059	0.2435	0.5742	0.068
H(8)	4*a*	0.9008	0.3608	0.4034	0.042
H(9)	4*a*	0.7373	0.5503	0.6459	0.126
H(10)	4*a*	0.6810	0.3879	0.5244	0.080
H(11)	4*a*	0.7265	0.1730	0.4197	0.065
H(12)	4*a*	0.8430	0.1042	0.2869	0.123
H(13)	4*a*	0.8471	0.0075	0.4843	0.113
H(14)	4*a*	0.8047	−0.1883	0.3053	0.144
H(15)	4*a*	0.7649	−0.1190	0.4094	0.100
H(16)	4*a*	0.7583	−0.0218	0.2083	0.163
H(17)	4*a*	0.8578	0.5805	0.7629	0.089
H(18)	4*a*	0.8617	0.6792	0.5921	0.064
H(19)	4*a*	0.8105	0.7093	0.6674	0.029

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)	4*a*	1.03914(3)	0.45033(7)	0.6682(1)	0.0308(3)	0.0265(2)	0.0238(2)	−0.0023(2)	−0.0017(2)	0.0011(3)
P(2)	4*a*	0.94465(3)	0.06601(7)	0.8746(1)	0.0266(3)	0.0255(2)	0.0316(3)	0.0026(2)	−0.0000(2)	0.0003(2)
O(1)	4*a*	0.97803(7)	0.4928(3)	0.7097(3)	0.0297(8)	0.049(1)	0.0315(9)	−0.0028(8)	−0.0019(7)	−0.0067(8)
O(2)	4*a*	1.06168(8)	0.3416(2)	0.8219(3)	0.041(1)	0.0376(9)	0.0372(9)	−0.0074(8)	−0.0105(8)	0.0116(7)
O(3)	4*a*	1.03816(8)	0.3563(2)	0.4981(3)	0.058(1)	0.0318(9)	0.0308(9)	0.0055(8)	−0.0026(9)	−0.0021(7)
O(4)	4*a*	1.07410(7)	0.6024(2)	0.6703(3)	0.0372(9)	0.0344(8)	0.0336(8)	−0.0071(7)	−0.0007(9)	0.0043(9)
O(5)	4*a*	0.90776(8)	0.2165(2)	0.9088(3)	0.0409(9)	0.0331(9)	0.038(1)	0.0096(7)	−0.0065(8)	−0.0076(7)
O(6)	4*a*	0.93964(8)	0.0510(3)	0.6724(3)	0.043(1)	0.073(1)	0.0361(9)	0.025(1)	−0.005(1)	−0.016(1)
O(7)	4*a*	0.91539(9)	−0.0795(3)	0.9628(5)	0.042(1)	0.038(1)	0.096(2)	0.0004(9)	0.012(1)	0.021(1)
O(8)	4*a*	1.00253(8)	0.0857(2)	0.9342(3)	0.0337(9)	0.0383(9)	0.0386(9)	0.0007(7)	−0.0049(8)	0.0102(8)
N(1)	4*a*	0.89047(9)	0.3399(3)	0.5093(3)	0.030(1)	0.044(1)	0.035(1)	−0.0056(9)	−0.0021(9)	0.003(1)
C(1)	4*a*	0.8299(1)	0.3527(4)	0.5182(4)	0.026(1)	0.056(2)	0.033(1)	−0.008(1)	−0.004(1)	0.010(1)
C(2)	4*a*	0.8004(1)	0.2223(4)	0.4473(5)	0.046(2)	0.058(2)	0.044(2)	−0.023(1)	−0.011(1)	0.012(1)
C(3)	4*a*	0.7428(2)	0.2424(5)	0.4569(6)	0.052(2)	0.096(3)	0.059(2)	−0.042(2)	−0.024(2)	0.024(2)
C(4)	4*a*	0.7189(1)	0.3782(7)	0.5275(6)	0.032(2)	0.103(3)	0.064(2)	−0.006(2)	−0.000(2)	0.021(2)
C(5)	4*a*	0.7501(2)	0.4967(5)	0.5923(6)	0.040(2)	0.098(3)	0.054(2)	0.009(2)	0.007(2)	0.013(2)
C(6)	4*a*	0.8074(1)	0.4910(5)	0.5930(5)	0.035(1)	0.062(2)	0.042(1)	−0.001(1)	0.002(1)	0.008(2)
C(7)	4*a*	0.8286(2)	0.0759(5)	0.3679(8)	0.073(3)	0.061(2)	0.080(3)	−0.023(2)	−0.024(3)	0.002(2)
C(8)	4*a*	0.7941(3)	−0.0656(6)	0.307(1)	0.164(6)	0.073(3)	0.106(5)	−0.034(3)	−0.050(4)	−0.001(3)
C(9)	4*a*	0.8412(1)	0.6279(5)	0.6730(7)	0.050(2)	0.067(2)	0.068(2)	0.006(2)	0.005(2)	−0.009(2)

Acknowledgment. We thank the Tunisian Secretary of State for Scientific Research and Technology for financial support.

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