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Synthesis and characterization of a new $(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)H_2XO_4$ (X = P, As)

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Abstract

Crystals of 2-amino-6-methylpyridinium dihydrogenmonophosphate (denoted as 2A6MPP) and 2-amino-6-methylpyridinium dihydrogenmonoarsenate (denoted as 2A6MPAs), have been prepared and grown at room temperature. They crystallize with triclinic unit cells and are isotopic. The following unit cell parameters were found, $(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)H_2PO_4$: $a = 7.5165(6)$, $b = 8.2640(5)$, $c = 8.5674(7)$ Å, $\alpha = 64.845(5)$, $\beta = 80.156(3)$, $\gamma = 85.783(5)$, $Z = 2$, $V = 474.61(6)$ Å^3; $(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)H_2AsO_4$: $a = 7.6011(4)$, $b = 8.4261(6)$, $c = 8.7074(6)$ Å, $\alpha = 64.228(3)$, $\beta = 81.047(4)$, $\gamma = 85.972(4)$, $Z = 2$, $V = 496.09(6)$ Å^3. The common space group is $P\bar{1}$. We have determined the structure of the phosphate. It exhibits infinite $(H_2PO_4)_n^{-n}$ chains. The organic groups $(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)^+$ are anchored between adjacent polyanions through multiple hydrogen bonds. The thermal property of the compound was investigated as well as was the IR property supported by group theoretical analyses.

Keywords: A. Inorganic compounds; B. Chemical synthesis; C. Differential scanning calorimetry (DSC); C. Infrared spectroscopy; C. X-ray diffraction

1. Introduction

The crystal chemistry of alkyl cations encapsulated between $[HXO_4]_n^{2n-}$ and $[H_2XO_4]_n^{n-}$ (X = P, As) polyanions is fascinating because it may lead to single crystals of polar materials. In these materials, the anions are observed to have a strong tendency to assemble via strong hydrogen bonds and build an infinite network such as chains [1–3], ribbons [4], layers [5,6], and three-dimensional networks [7]. A compromise between dimension and charge of anion is decisive for reaching an acentric crystal useful for quadratic non linear optical behavior. This compound was synthesized within a systematic search on new materials resulting from the association of organic and inorganic entities, which could be of particular interest in non linear optics [8]. The compound formula $(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)H_2PO_4$ is abbreviated as 2A6MPP, the crystal structure, the thermal behavior and the IR results are discussed.

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2. Experimental

2.1. Chemical preparation

Two aqueous solutions (10^{-1} M) of phosphoric and arsenic acids were separately neutralized with a solution of 2-amino-6-methylpyridine. Evaporation of the resulting solutions, at room temperature for several weeks, leads to transparent parallelepipedic single crystals. The morphology of the phosphate crystals is close to that of the arsenate. The chemical preparations, run at room temperature, are successfully reproduced according to the chemical reaction:

$$(2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_3N) + H_3XO_4 \xrightarrow[H_2O]{X=P,As} (2\text{-}NH_2\text{-}6\text{-}CH_3C_5H_4N)H_2XO_4$$

The crystals obtained in this way are pure and stable under normal conditions of temperature and humidity.

2.2. Characterization techniques

2.2.1. X-ray diffraction

The main crystal data, the parameters used for the intensity data collection and the final results are summarized in Table 1 for 2A6MPP.

Table 1
Crystallographic data and structure refinement for 2A6MPP

	2A6MPP
Formula weight (g mol^{-1})	206.14
Crystal system	Triclinic
Space group/Z	$P\bar{1}/2$
Lattice parameters at 298 K	$a = 7.5165(6)$ Å, $\alpha = 64.845(5)^\circ$ $b = 8.2640(5)$ Å, $\beta = 80.156(3)^\circ$ $c = 8.5674(7)$ Å, $\gamma = 85.783(5)^\circ$
Volume (Å^3)	474.61(6)
Density (g/cm^3)	1.442
Absorption coefficient μ (mm^{-1})	0.276
$F(0\,0\,0)$	216
Crystal dimensions (mm^3)	$0.29 \times 0.21 \times 0.15$
Diffractometer	Kappa CCD Nonius
Wavelength	Mo Kα ($\lambda = 0.71073$ Å)
$\theta_{min.}/\theta_{max.}$ (°)	3.70/26.31
h, $\pm k$, $\pm l$ range	0/9, 9, 10
Number of measured reflections	1732
Number of independent reflections	1469
Observed reflections ($I > 2\sigma I$)	1469
Data reductions programs	Denzo [9]
Programs used	SHELXS-97 [10] SHELXL-97 [10]
Absorption correction	None
Refinement method	Full matrix of F^2, least squares fit
Number of refined parameters	163
Goodness-of-fit[a] (S)	1.056
Residuals[a]	$R_1 = 0.0371$, $wR_2 = 0.0915$
Residuals (all data)[a]	$R_1 = 0.0371$, $wR_2 = 0.0915$
Extinction coefficient ε	0.22(5)
$\Delta\rho_{min.}/\Delta\rho_{max.}$ (e/Å^3)	−0.266/0.408

[a] Definitions according to [9].