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Materials Research Bulletin 40 (2005) 2243–2255

Materials Research Bulletin

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Crystal structure, thermal analysis and IR spectroscopic investigation of $(C_6H_9N_2)H_2XO_4$ (X = As, P)

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Received 2 June 2005; accepted 22 June 2005
Available online 20 July 2005

Abstract

Crystals of 2-amino-4-methylpyridinium dihydrogenmonoarsenate $(C_6H_9N_2)H_2AsO_4$ and 2-amino-4-methylpyridinium dihydrogenmonophosphate $(C_6H_9N_2)H_2PO_4$ have been prepared and grown at room temperature. These materials are isotypic with the following unit cell dimensions $(C_6H_9N_2)H_2AsO_4$: $a = 12.4415(5)$ Å, $b = 6.8224(3)$ Å, $c = 11.3524(5)$ Å, $Z = 4$, $V = 963.60(6)$ Å^3; $(C_6H_9N_2)H_2PO_4$: $a = 12.4410(9)$ Å, $b = 6.7165(3)$ Å, $c = 11.3417(5)$ Å, $Z = 4$, $V = 925.09(10)$ Å^3. The common space group is *Pnma*. The structure of these compounds has been determined by X-ray data collection on single crystals of $(C_6H_9N_2)H_2AsO_4$ and $(C_6H_9N_2)H_2PO_4$. Due to the strong hydrogen-bond network connecting the H_2XO_4 groups, the anionic arrangement must be described as a linear organization. The chains composed by the $(H_2XO_4)_n^{n-}$ macroanion spread along the *b*-direction, approximately centered by $x = 0$ and 1/2. All atoms of the structure, except one oxygen atom, are located in the mirror planes situated at $y = 1/4$ and 3/4, imparting an internal mirror symmetry to the anionic and the cationic entities. The linear macroanions are crossed by organic cations lying in mirrors perpendicular to the *b*-direction; this atomic arrangement is then described by a three-dimensional network of hydrogen bonds, built up by two types, $\underline{\mathbf{O}}\text{–}\underline{\mathbf{H}}\cdots\underline{\mathbf{O}}$ bonds inside the chains and $\underline{\mathbf{N}}\text{–}\underline{\mathbf{H}}\cdots\underline{\mathbf{O}}$ bonds linking adjacent chains. The thermal properties of both compounds are investigated as well as the IR properties supported by group theoretical analyses.

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

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doi:10.1016/j.materresbull.2005.06.006

1. Introduction

The As and P atoms, belonging to the same group, have similar properties, in particular, the interaction of arsenic and phosphoric acids with organic molecules which gives rise to new materials with similarity in structures and physical properties. The two isotypic compounds $C_5H_6N_3O_2^+{\cdot}H_2PO_4^-$ [1] and $C_5H_6N_3O_2^+{\cdot}H_2AsO_4^-$ [2] exhibit non-linear optical properties, while the series of compounds $C_nH_{2n+1}NH_3^+{\cdot}H_2PO_4^-$ (n = 1–9, 12) and $C_nH_{2n+1}NH_3^+{\cdot}H_2AsO_4^-$ (n = 6–8) reveal the existence of phase transitions and some of the phases are ferroelectric [3,4]. It is worth noting that the importance of the hydrogen-bond pattern is responsible for the occurrence of ferroelectricity and phase transitions in such compounds. On the other hand, the difference in reactivity between the two XO_4 groups is enormous; the oxanions with arsenic, AsO_4, are reactive while those of phosphorous are stable and unreactive. Nevertheless, the important role of phosphoric acid and its derivatives in biochemical processes is well known. Furthermore, many biochemical properties seem to be due to the ability of arsenic (V) to mimic the analogous phosphates [5]; arsenate may substitute for phosphate as a substrate in certain phosphorylation reaction [6]. The aim of the present work is devoted to a detailed structural investigation of the two isostructural compounds, $(C_6H_9N_2)H_2AsO_4$ (I) and $(C_6H_9N_2)H_2PO_4$ (II), located in the system H_3XO_4–ORG, where X = As, P and ORG = 2-amino-4-methylpyridine. Thermal behavior and IR spectra of these two new compounds are discussed.

2. Experimental

Two aqueous solutions (10^{-1} M) of arsenic and phosphoric acids were separately neutralized with an aqueous solution of 2-amino-4-methylpyridine. Evaporation of the resulting solutions, at room temperature for several weeks, leads to transparent parallelepipedic single crystals of (I) and (II). The morphology of the arsenate crystals is close to that of the phosphate. The chemical preparations, run at room temperature, are successfully reproduced according to the chemical reactions:

$$C_6H_8N_2 + H_3AsO_4 \xrightarrow{H_2O} (C_6H_9N_2)H_2AsO_4$$

$$C_6H_8N_2 + H_3PO_4 \xrightarrow{H_2O} (C_6H_9N_2)H_2PO_4$$

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

X-ray intensity data of (I) and (II) were collected on a Nonius Kappa CCD diffractometer using monochromated Mo Kα radiation with a specimen-to-image plate distance of 2.7 cm. Ninety frames were recorded with a count scan rate of 2° in φ every 120 s. The first 10 frames were used for indexing the reflections and refining the cell parameters by using the Denzo [7] package. The structure of (I) is first solved with a direct method, from the SHELXS-97 [8], which permitted the location of the AsO_4 group. The other non-hydrogen atoms were rapidly located after subsequent cycles of refinement and difference Fourier synthesis using the SHELXL-97 program [9]. The reliability R decreases to 3.26% (R_w = 8.47%) in the final least-squares refinement of atomic parameters with isotropic thermal factors for the H atoms. Using data collected on crystal of (II), the structure resolution with the same