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Crystal structure and vibrational spectra of melaminium arsenate

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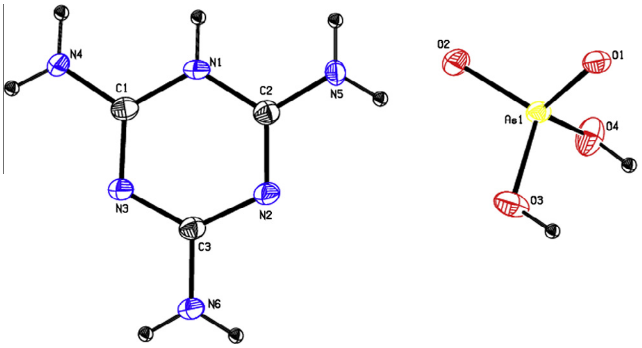
HIGHLIGHTS

- Synthesized by slow solvent evaporation method.
- X-ray crystallographic study has been carried out.
- Crystallizes in triclinic system with space group P−1.
- Vibrational spectral analysis has been done.
- No phase transition in the studied temperature range (113–293 K).

GRAPHICAL ABSTRACT



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ABSTRACT

The crystals of the new melaminium arsenate (MAS) $[C_3H_7N_6^+ \cdot H_2AsO_4^-]$ were obtained by the slow evaporation of an aqueous solution at room temperature. Single crystal X-ray diffraction analysis reveals that the crystal belongs to triclinic system with centro symmetric space group P−1. The crystals are built up from single protonated melaminium residues and single dissociated arsenate $H_2AsO_4^-$ anions. The protonated melaminium ring is almost planar. A combination of ionic and donor–acceptor hydrogen-bond interactions linking together the melaminium and arsenate residues forms a three-dimensional network. Vibrational spectroscopic analysis is reported on the basis of FT-IR and FT-Raman spectra recorded at room temperature. Hydrogen bonded network present in the crystal gives notable vibrational effect. DSC has also been performed for the crystal shows no phase transition in the studied temperature range (113–293 K).

Introduction

The present study is a continuation of our investigations on characterization of melamine based crystals in the solid state. Melamine and its derivatives of organic and inorganic complexes or salts can develop well defined non-covalent supramolecular architectures via multiple hydrogen bonds, since they contain complementary arrays of hydrogen bonding sites [1,2]. Melamine, 2,4,6-triamino-1,3,5-triazine, was obtained for the first time by Liebig in the year 1834 [3]. Melamine readily forms insoluble adducts with many organic and inorganic acids. Melamine and its salts like melamine cyanurate, melaminium orthophosphate has a wide industrial application as fire retardant substance. Melamine resin is used in automobile paints, which were examined by Zięba-Palus [4]. Melamine forms supramolecular networks by hydrogen bonding [5–8].

Recently, the synthesis and structure of a copper (II) melamine complex with direct Cu-melamine coordination were published [9]. Such a molecular self-assembled arrangement was intensively

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studied by different techniques including solid state NMR [10]. Vibrational and thermal characterization of supramolecular structures is helpful to unravel the principles of molecular self-assembly. Orthoarsenic acid (H_3AsO_4) forms interesting complexes with organic cations.

The association of organic moieties with inorganic residues has been proposed for the preparation of nonlinear optical materials. The structural phase transitions are common features for arsenates. The intense hydrogen-bonded systems formed in these salts were widely investigated as responsible for structural changes occurred. We also were interested in vibrational spectra for melamine arsenate crystal among others due to hydrogen bond system present in this crystal.

The detailed assignment of the bands on the basis of infrared and Raman polarized spectra [11] as well as the discussion of internal fundamental vibrations of KH_2AsO_4 in the paraelectric phase [12] were already published. Ilczyszyn et al. [13] published the results of polarized infrared and Raman studies for urea-arsenic acid single crystals. Moreira et al. [14] described lattice dynamics in this system. For betaine arsenate, Ilczyszyn and Ratajczak [15] performed the complete vibrational room temperature polarized single crystal examination. Ilczyszyn [16] provided the spectral evidences for the structural changes in this interesting crystal on the basis of low temperature polarized single crystal measurements while Yuzyuk et al. [17] studied in detail the soft-mode mechanism of the order–disorder type of ferroelectric phase transition. Mielke et al. [18] discussed the force constants and vibrational frequencies of orthoarsenates.

It seemed that vibrational (IR and Raman) spectroscopy would be a suitable method to study hydrogen-bonded organo-mineral complexes in crystalline form. So far, some new non-linear optical crystals of non-centrosymmetric structures based on hydrogen bond interactions were discovered [19,20]. Some salts of arsenous acid exhibit nonlinear optical properties, namely second harmonic generation. This phenomenon was already observed and its efficiency determined for the powder sample of the L-lysine-arsenous acid [21] using the Kurtz-Perry method as described in [22]. Centrosymmetric structure without second harmonic generation was revealed for anilinium arsenate [23].

Paraelectric–ferroelectric type of transition was already studied for potassium dihydrogen arsenate, rubidium dihydrogen arsenate and cesium dihydrogen arsenate [24]. Moreira et al. [25] performed Raman scattering study of the phase transition sequence in the mixed system of betaine arsenate and deuterated betaine arsenate ($BA_{(1-x)}DBA_x$). Hatori et al. [26] discovered an interesting hybrid organic/inorganic arrangement, dimethylammonium dihydrogen arsenate. According to dielectric, AC calorimetric and X-ray investigations, the second-order ferroelectric phase transition at 274.5 K occurred in this crystal. To the best of our knowledge, no X-ray crystallographic data and vibrational spectral studies of this MAS $[C_3H_7N_6^+ \cdot H_2AsO_4^-]$ molecule has not yet been published. The aim of this paper is to study the structure and vibrational spectroscopic behavior of MAS crystal in detail.

Experimental

The starting compounds, melamine (Aldrich, 99%) and As_2O_5 (Aldrich, 95 %) were used as supplied and prepared in the ratio of 1:1. The dissolved As_2O_5 was added dropwise to the hot solution of melamine and stirred well. After the solution (pH = 7) was cooled to room temperature, it remained clear. Then, the solution was additionally purified with the aid of active charcoal. The solution slowly evaporated over the course of a few days till the colourless and transparent needle like (2–3 cm long) crystals appeared. The photograph of as-grown single crystals of MAS is shown in Fig. 1.

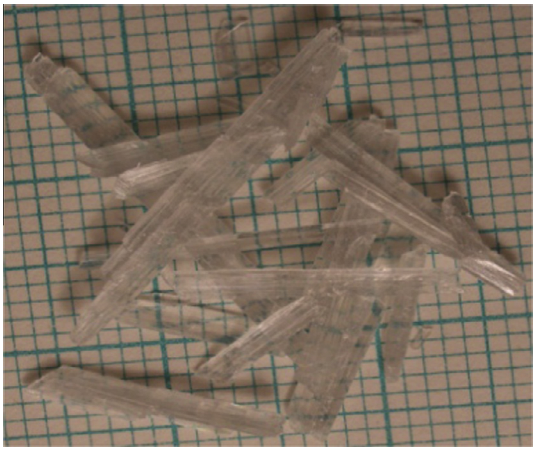

Fig. 1. Photograph of as-grown MAS crystals.

Results and discussion

Crystal structure analysis

A crystal of dimension (0.26 × 0.22 × 0.20 mm) was sealed in a capillary tube and intensities collected at room temperature 293(2)K using a four circle KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector. The graphite monochromatized Mo Kα (λ = 0.71073 Å) and ω-scan technique with $\Delta\omega$ = 0.75° for one image were used for data collection. Integration of the intensities, correction for Lorentz and polarization effects were performed using a KUMA-KM-4 CCD software [27]. The face-indexed analytical absorption was calculated using the SHELXL program [28], the maximum and minimum transmission factors being 0.4418 and 0.5205. About 2239 reflections were collected with independent reflections, R_{int} = 0.0248 were used for structure solution and refinement. The structure was solved by a direct method and subsequent difference Fourier syntheses of SHELXL-PLUS program system [28] and the structure refinement was done by use of SHELXL 97 [29]. Anisotropic displacement parameters were included for all non hydrogen atoms. The crystal data and structure refinement parameters are given in Table 1. The molecular structure (ORTEP diagram) of MAS is shown in Fig. 2. The packing diagram of MAS is shown in Fig. 3. The various hydrogen bond geometrical parameters are presented in Table 2 along with symmetry codes. Selected bond distances and bond angles are compiled in Table 3. Atomic displacement parameters, fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) are listed in Tables 4 and 5. MAS crystal crystallizes in the triclinic system with centrosymmetric space group P−1 and the calculated lattice parameters are a = 4.733(10) Å, b = 9.325(2) Å, c = 10.405(2) Å, α = 82.65(3)°, β = 87.81(3)°, γ = 84.34(3)° and V = 453.08(16) (Å)^3. The asymmetric unit of MAS consists of two well defined oppositely charged residues; a protonated moiety at one of the three N atoms of the melamine ring and a H atom (or H atoms) of the $H_2AsO_4^-$ arsenate ion. The ring of the melaminium residue is significantly distorted from the ideal hexagonal from. The average ring and terminal C–N bond distances are 1.36 Å and 1.33 Å respectively. The internal C1–N3–C3 (115.8°) and C2–N2–C3 (114.7°) angles of the melamine ring are smaller than the C1–N1–C2 (119.8°) angle at the protonated N atom. These differences are due to the steric effect of an electron lone pair and are fully consistent with the valence shell electron-pair-repulsion theory [30,31]. The similar situation is observed in the crystal structure of other reported mono protonated melaminium cations [32]. The internal N–C–N angles [N1–C1–N3 (121.3°),