

The values of the profile parameters  $U$ ,  $V$  and  $W$  obtained after refinement (Table 2) are significantly higher than those calculated theoretically (Table 1). The effect of such differences on the full widths at half maximum (fwhm) is illustrated in Fig. 2. This type of discrepancy between theoretical predictions and experimental results has been observed previously (Caglioti & Ricci, 1962) and could be attributed to a number of causes, including crystallite size broadening of the diffracted peaks. However, crystallites of distinct crystal habits (such as lath-like, needle-like, *etc.*) and of dimensions sufficiently small to produce line broadening would affect the widths of some diffraction peaks much more than those of others, changing radically the relationship between the fwhm  $H$  and the diffraction angle  $\theta$  and thus making the application of Rietveld's method impossible. On the other hand, it is possible to show that crystallites of spherical or approximately spherical shape do not alter the form of the function  $H(\theta)$  and the value of the parameter  $V$  but change the values of

the parameters  $U$  and  $W$  by equal increments. Since we have for our case  $|V_{\text{calc}}| < |V_{\text{exp}}|$  (see Tables 1 and 2), it must be concluded that the differences between the observed and calculated values of  $U$ ,  $V$  and  $W$  cannot be attributed to crystallite size effects but rather to inappropriate or incomplete assumptions in the original theory.

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*Acta Cryst.* (1977). **B33**, 3947–3949

### Triammonium Orthoarsenate Trihydrate

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(Received 15 May 1977; accepted 3 August 1977)

**Abstract.**  $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 6.818$  (7),  $b = 6.364$  (5),  $c = 22.811$  (21) Å,  $\beta = 93.74$  (6)° (Syntex  $P\bar{1}$  autodiffractometer),  $Z = 4$ ,  $V = 987.7$  Å<sup>3</sup>, FW 247.08,  $D_c = 1.66$ ,  $D_m = 1.61$  g cm<sup>-3</sup> (by flotation at ~4°C). The crystals were grown at ~4°C in a sealed flask by neutralizing concentrated  $\text{H}_3\text{AsO}_4$  solution with KOH followed by addition of a large excess of  $\text{NH}_4\text{OH}$  solution. The crystal is isostructural with the corresponding phosphate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ . The averaged As–O bond length is 1.685 Å. The compound loses  $\text{NH}_3$  gradually on exposure to the atmosphere at room temperature and finally converts to  $(\text{NH}_4)_2\text{HASO}_4$ .

**Introduction.** Crystals of  $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$  (TAA) are transparent and plate-like. The crystal to be studied was sealed in a Lindemann-glass capillary. The intensity data of 1127 independent reflexions ( $>3\sigma$ ,  $\sin \theta/\lambda < 0.56$  Å<sup>-1</sup>) were collected on a Syntex  $P\bar{1}$  autodiffractometer using Cu  $K\alpha$  (Ni) radiation. The intensities were converted to  $F_o$  values after applying Lorentz–polarization, absorption and time-decay corrections. Intensity data from azimuthal rotation about the two strong

reflexions, 200 and 400, were used for the absorption correction (North, Phillips & Mathews, 1968). The linear absorption coefficient for Cu  $K\alpha$  radiation is 50.9 cm<sup>-1</sup>. Time-decay corrections were made from intensity data of three check reflexions remeasured periodically. Total deterioration of the check reflexions ranged from 8.5 to 9.5%.

The cell-dimension data and space group indicate that TAA is isomorphous with the corresponding phosphate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$  (TAP) (Mootz & Wunderlich, 1970). This was confirmed from Patterson and Fourier syntheses. The non-H coordinates of TAP [except the split O(7) atom] were then used for the initial refinement of the TAA structure by the full-matrix least-squares method; this gave an  $R$  value of 0.14. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $F_c$  and  $F_o$  are the calculated and observed structure factors, respectively, and  $w$  is the weight. The weighting scheme of Stout & Jensen (1968) was used. A difference Fourier map (DFM) calculation at this stage indicated O(7) could be disordered. Nonetheless, the refinement using anisotropic thermal parameters and assuming a split O(7) atom similar to that in TAP gave no better



The influence on these structures of the replacement of a  $P^{5+}$  ion by an  $As^{5+}$  ion has also been discussed (Khan *et al.*, 1972; Khan & Baur, 1973).

The structure of TAA is isomorphous with that of TAP. The reasons for the justification of the stoichiometric coexistence of  $NH_4^+$  and  $XO_4^{3-}$  in TAP (Mootz & Wunderlich, 1970) thus also apply to TAA.

The shape of the  $AsO_4$  group deviates slightly from ideal tetrahedral. Each O atom participates in three hydrogen bonds, except O(2) which forms four [accordingly, As—O(2) is longer]. The shorter As—O(4), however, could be the result of hydrogen bonding of O(4) to the three-coordinated O(7). The averaged As—O bond distance is 1.685 Å, longer than that found in  $Na_3AsO_4 \cdot 12H_2O$ , 1.669 Å (Tillmanns & Baur, 1971). The corresponding values found in ADA and DAA are 1.682 and 1.695 Å respectively.

The tetrahedral  $AsO_4^{3-}$  anions and the  $NH_4^+$  cations of N(1) and N(2) are hydrogen bonded into arrays of infinite columns with twofold screw symmetry. Additional hydrogen bonds provided by the rest of the  $NH_4^+$  ions and  $H_2O$  molecules link these arrays of columns into a unique hydrogen-bonding network (Fig. 1). All  $NH_4^+$  ions and  $H_2O$  molecules are four coordinated, except O(7).

O(7) could be in a disordered state (dynamic or static) as suggested by its abnormally large thermal parameters. O(5), which hydrogen bonds to O(7) and has larger thermal parameters, may also be in a disordered state. The root-mean-square (r.m.s.) components of thermal displacements along the principal axes are 0.174, 0.226 and 0.457 Å for O(7) and 0.158, 0.220 and 0.258 Å for O(5). The largest r.m.s. component of thermal displacement of O(7) (0.457 Å) is almost perpendicular to the O(5)—O(7)—O(4) plane (the angle between the principal axis and vector is  $19.9^\circ$ ), while that of O(5) (0.258 Å) is almost along the O(5)—O(7) direction ( $25.9^\circ$ ). The hydrogen-bond distances involving these two O atoms are all significantly longer or shorter than those involving O(6) (Fig. 2). The hydrogen-bond lengths between O atoms

of the  $AsO_4$  group and  $NH_4^+$  ions N(1) and N(2) range from 2.789 to 2.819 Å. N(3)···O(2) is significantly longer (2.852 Å). These hydrogen-bond lengths in TAA are about equal to or slightly greater than the corresponding values in TAP.

TAA gradually loses  $NH_3$  on exposure to the atmosphere at room temperature. Further dehydration results in a compound which was identified as DAA by cell-dimension and space-group determinations. A similar observation of the conversion of TAP into DAP has previously been studied by thermographic analysis (Nabiev, Saibova, Borukhov & Parpiev, 1969). This indicates TAP loses one molecule of  $NH_3$  easily.

This work is supported in part by the National Science Council of the Republic of China. We thank Professor T. J. Lee for help in data collection.

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