The values of the profile parameters U, V and Wobtained 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 θ 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 $|V_{calc}| < |V_{exp}|$ (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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Triammonium Orthoarsenate Trihydrate

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Abstract. $(NH_4)_3AsO_4.3H_2O$, monoclinic, $P2_1/c$, a = 6.818 (7), b = 6.364 (5), c = 22.811 (21) Å, $\beta = 93.74$ (6)° (Syntex PI autodiffractometer), Z = 4, V = 987.7 Å³, FW 247.08, $D_c = 1.66$, $D_m = 1.61$ g cm⁻³ (by flotation at ~4°C). The crystals were grown at ~4°C in a sealed flask by neutralizing concentrated H₃AsO₄ solution with KOH followed by addition of a large excess of NH₄OH solution. The crystal is isostructural with the corresponding phosphate, (NH₄)₃-PO₄.3H₂O. The averaged As-O bond length is 1.685 Å. The compound loses NH₃ gradually on exposure to the atmosphere at room temperature and finally converts to $(NH_4)_2HAsO_4$.

Introduction. Crystals of $(NH_4)_3AsO_4$. $3H_2O$ (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 $(>3\sigma, \sin\theta/\lambda < 0.56 \text{ Å}^{-1})$ were collected on a Syntex $P\bar{I}$ 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⁻¹. 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, (NH₄)₃PO₄. 3H₂O (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 leastsquares 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

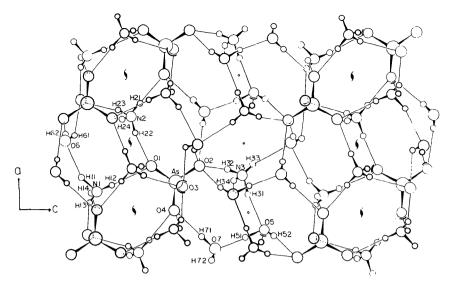
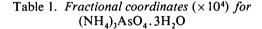


Fig. I. Packing diagram (projection onto the ac plane). Thin lines indicate hydrogen bonds.



| | | | | X/A | ¥/8 | 2/0 | | | |
|-----|-------|------|-------|---------|----------|----------|------|------|------|
| | | A | 5 20 | 38(1) | 3615(1) | 3427(0) | | | |
| | | 0 | 30 | 50(8) | 43961 91 | 2808(2) | | | |
| | | Ď. | 3 3 3 | 071 8) | 46441 91 | 4026(2) | | | |
| | | 01 | 20 | 90(7) | 979(10) | 3485(2) | | | |
| | | 04 | : | 85(7) | 4461(8) | 3409(2) | | | |
| | | 0 | 5 -12 | 21(9) | 2594(10) | 5279(3) | | | |
| | | 0 | 5 49 | 83(8) | 3514(8) | 1026(3) | | | |
| | | 0 | 7 -28 | 307(10) | 3313(18) | 4200(4) | | | |
| | | N | L 14 | 02(10) | 3678(10) | 1665(3) | | | |
| | | N. | 2 68 | 386(10) | 3638(10) | 24991 31 | | | |
| | | N | 3 20 | 505(10) | 1737(11) | 4941(3) | | | |
| | x/A | ¥78 | 210 | в | | X/A | ¥/8 | 2/0 | в |
| н11 | 2393 | 4050 | 1406 | 3.00 | H12 | 1990 | 3627 | 2056 | 3.00 |
| H13 | 405 | 4714 | 1642 | 3.00 | H14 | 870 | 2350 | 1561 | 3.00 |
| H21 | 7987 | 3922 | 2766 | 3.00 | H22 | 5714 | 3910 | 2671 | 3.00 |
| H23 | 6991 | 4496 | 2156 | 3.00 | H24 | 6945 | 2196 | 2380 | 3.00 |
| H31 | 1494 | 2267 | 5112 | 3.00 | H32 | 2915 | 2569 | 4615 | 3.00 |
| н33 | 3705 | 1714 | 5222 | 3.00 | H34 | 2357 | 323 | 4810 | 3.00 |
| H51 | -2150 | 2958 | 4965 | 3.00 | H52 | -1176 | 3534 | 5603 | 3.00 |
| H61 | 6110 | 4211 | 1198 | 3.00 | H62 | 5138 | 2027 | 1075 | 3.00 |
| H71 | -1441 | 3560 | 4186 | 3.00 | H72 | -3490 | 4615 | 4181 | 3.00 |

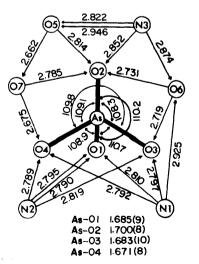


Fig. 2. The hydrogen-bonding scheme, hydrogen-bond lengths and the interatomic bond lengths (Å) and angles (°) of the AsO_4^{3-} ion.

R value than that using a nonsplit model, which gave an *R* of 0.10. After an extinction correction, a DFM was calculated which revealed most of the expected H atom positions. The H atom positions to be used in the final refinement as fixed contributions were either those obtained from the DFM or those calculated using N-H and O-H bond lengths of 0.95 Å, and H-N-H and H-O-H bond angles of 109.5°.

The final full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms converged to an R value of 0.07. The extinction coefficient, C' [equation (5) in Zachariasen (1968)], was 4.8×10^{-6} . Atomic scattering factors and the dispersion correction $\Delta f'$ for the As atom with Cu K α radiation were all taken from International Tables for X-ray Crystallography (1962).

The final coordinates are shown in Table 1.* The crystal packing (projection onto the *ac* plane) is shown in Fig. 1. Fig. 2 gives the hydrogen-bonding scheme, the hydrogen-bond lengths, and the bond distances and angles of the AsO_4^{3-} group.

Discussion. The crystal structures of $NH_4H_2PO_4$ (ADP) (Khan & Baur, 1973; Tenzer, Frazer & Pepinsky, 1958), $NH_4H_2AsO_4$ (ADA) (Khan & Baur, 1973), $(NH_4)_2HPO_4$ (DAP) (Khan, Roux & James, 1972), $(NH_4)_2HAsO_4$ (DAA) (Khan, Straumanis & James, 1970) and TAP (Mootz & Wunderlich, 1970) have previously been determined. ADA and DAA are shown to be isostructural with ADP and DAP respectively.

^{*} Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32917 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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 AsO₄ 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 Na₃AsO₄. 12H₂O, 1.669 Å (Tillmanns & Baur, 1971). The corresponding values found in ADA and DAA are 1.682 and 1.695 Å respectively.

The tetrahedral AsO₄³⁻ anions and the NH₄⁺ 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 NH₄⁺ ions and H₂O molecules link these arrays of columns into a unique hydrogen-bonding network (Fig. 1). All NH₄⁺ ions and H₂O 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°), while that of O(5) (0.258 Å) is almost along the O(5)-O(7) direction (25.9°). 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 AsO₄ group and NH⁴₄ 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 celldimension 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.

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