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The Crystal Structure of Diammonium Hydrogen Arsenate, $(NH_4)_2HAsO_4$*

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$(NH_4)_2HAsO_4$ is monoclinic, space group $P2_1/c$, with cell constants $a=11{\cdot}378$ (5), $b=6{\cdot}908$ (6), $c=8{\cdot}129$ (5) Å, $\beta=113{\cdot}0$ (2)° and $Z=4$. The crystal structure has been determined from Weissenberg film data using Patterson and Fourier syntheses and refined with individual isotropic temperature factors by the least-squares method employing three-dimensional data (607 structure factors). The final R value, without the hydrogen atoms (which were not located), is 0·086. The $(AsO_3OH)^{2-}$ and NH_4^+ groups are held together by hydrogen bonds. The length of the O–H···O bond is 2·669 Å. There are five oxygen atoms around each of the two nitrogen atoms with N···O distances between 2·78 and 3·09 Å. Each of these contacts may be involved in hydrogen bonding.

Introduction

During the course of X-ray studies on some KH_2PO_4-type compounds (Khan, 1966) crystals of ammonium dihydrogen arsenate, $NH_4H_2AsO_4$, were prepared by evaporating a mixture of liquid ammonia and an aqueous solution of As_2O_5. It was noticed that crystals of [diammonium hydrogen arsenate, $(NH_4)_2HAsO_4$, were obtained instead if ammonia was present in excess. In view of the considerable interest in hydrogen bonding in crystalline materials, it was decided to determine the structure of this acid salt, which has nine hydrogen atoms per formula unit.

Experimental

Crystals of $(NH_4)_2HAsO_4$ grow plate-like, and it is possible to recognize the $2/m$ symmetry morphologically. Samples were prepared for X-ray studies by cutting a crystal of about $5\times5\times2$ mm and rolling this piece between fine emery papers until a cylinder of diameter 0·18 mm with its length along the twofold axis was obtained. It was necessary to shellac the specimen to avoid decomposition of the compound, otherwise powder lines appeared on single-crystal photographs within a few hours of its contact with the atmosphere. Oscillation and Weissenberg photographs were taken with a Weissenberg camera, the radius of which was calibrated with powder lines, obtained at about 25 °C from a commercial sample of CdO; the lattice constant of CdO at this temperature is $4{\cdot}6951\pm0{\cdot}0001$ Å, as determined by Khan (1966). Intensity data were collected for $h0l$, $h1l$, $h2l$ and $h3l$ reflections by the multiple film method, employing Cu $K\alpha$ radiation. The total number of observed reflections was 619 and there were 58 absent reflections. The intensities were converted to F_o values on an IBM 360/50 computer after applying the Lorentz-polarization, absorption and spot-shape corrections. Standard data given in *International Tables for X-ray Crystallography* (1959) were used for Lorentz–polarization and absorption corrections. The spot-shape corrections were made as follows. The extended spots on the higher layers vary in length with $Y/2$, where Y is the projection of the angle between the incident and reflected beam onto the zero layer. When ratios of the lengths of these spots to the spots on the zero layer were plotted against sin $Y/2$, a smooth curve was obtained. Fifteen to twenty spots were sufficient to determine the curve which was then used for corrections at any particular value of $Y/2$ by the usual interpolation method. Three other programs used during the course of this structure work are the following: Fourier-synthesis program *FORDAP* written by Allan Zalkin; Least-squares program *ORFLS* by Busing, Martin & Levy (1962); and the program *SADIAN* written by Werner Baur for the calculation of bond distances and bond angles. Atomic scattering factors and the dispersion corrections $\Delta f'$ and $\Delta f''$ for the As atom with Cu $K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1962).

Crystal data

Diammonium hydrogen arsenate is monoclinic with $a=11{\cdot}378$ (5)*, $b=6{\cdot}908$ (6), $c=8{\cdot}129$ (5) Å, $\beta=113{\cdot}0$ (2)°; $V=584$ (1) Å^3, $Z=4$, $\varrho_c=2{\cdot}00$ g.cm^{-3}, $\varrho_m=1{\cdot}989$ g.cm^{-3} (Schiff, 1859); the formula weight is 175·92. The standard deviations of the lattice constants were estimated by repeated measurements of the calibrated films. The space group, chosen as $P2_1/c$ from the systematic absences ($h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$), was proved to be correct by the successful refinement of the structure.

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* Throughout this paper the estimated standard deviations are given in parentheses following the value. They show the uncertainty of the least significant digit.

Structure determination

The structure was determined from Patterson and Fourier syntheses and was refined by the method of least-squares using Hughes's (1941) weighting scheme. The refinement was carried out with the 58 absent reflections included with $I_{min}/2$ as their intensities, and by removing the strong reflections which were estimated with limited accuracy. The final R value for the 607 reflections, with individual isotropic temperature factors, converged to 0·086. Since the intensity data were all collected with the crystal mounted along the b axis, in Weissenberg geometry, there would be complete correlation between the scale factors of the higher layer data and the coefficients β_{22}, and consequently, an anisotropic refinement is not reported here. Attempts to locate the hydrogen atoms from difference syntheses were not successful.

Atomic coordinates and thermal parameters are listed in Table 1 and the observed and calculated structure factors are compared in Table 2. Absent reflections included in the refinement are indicated by the letter A and the strong reflections omitted from the refinement are indicated by asterisks.

Discussion of the structure

A three-dimensional view of the structure is shown in Fig. 1. The interatomic distances and angles with their standard deviations are given in Table 3. The structure consists of $(AsO_3OH)^{2-}$ and NH_4^+ groups held together by hydrogen bonds. The AsO_4 tetrahedra are connected by O–H..O bonds in such a way that the hydrogen bonds link the oxygen atom O(1) from one AsO_4 unit to O(4) of the neighboring unit to form an infinite zigzag chain along the **c** direction. The oxygen atoms of

Table 1. $(NH_4)_2HAsO_4$, *Positional and thermal parameters with their standard deviations*

	x	y	z	B
As	0·2495 (2)	0·8910 (3)	0·4285 (1)	2·25 (5) Å^2
O(1)	0·2083 (7)	0·9865 (22)	0·2142 (9)	2·93 (13)
O(2)	0·2599 (7)	0·0974 (16)	0·5438 (10)	2·52 (14)
O(3)	0·3870 (6)	0·7682 (18)	0·4968 (8)	2·46 (13)
O(4)	0·1314 (6)	0·7459 (15)	0·4293 (8)	2·16 (12)
N(1)	0·4480 (8)	0·1186 (19)	0·1535 (11)	2·68 (16)
N(2)	0·1210 (8)	0·3774 (19)	0·2626 (11)	2·72 (16)

Table 2. *Observed and calculated structure factors* ($\times 5$)

The sign of the real part of F_o is given. The letter A indicates absent reflection and an asterisk indicates a strong reflection omitted from the refinement.

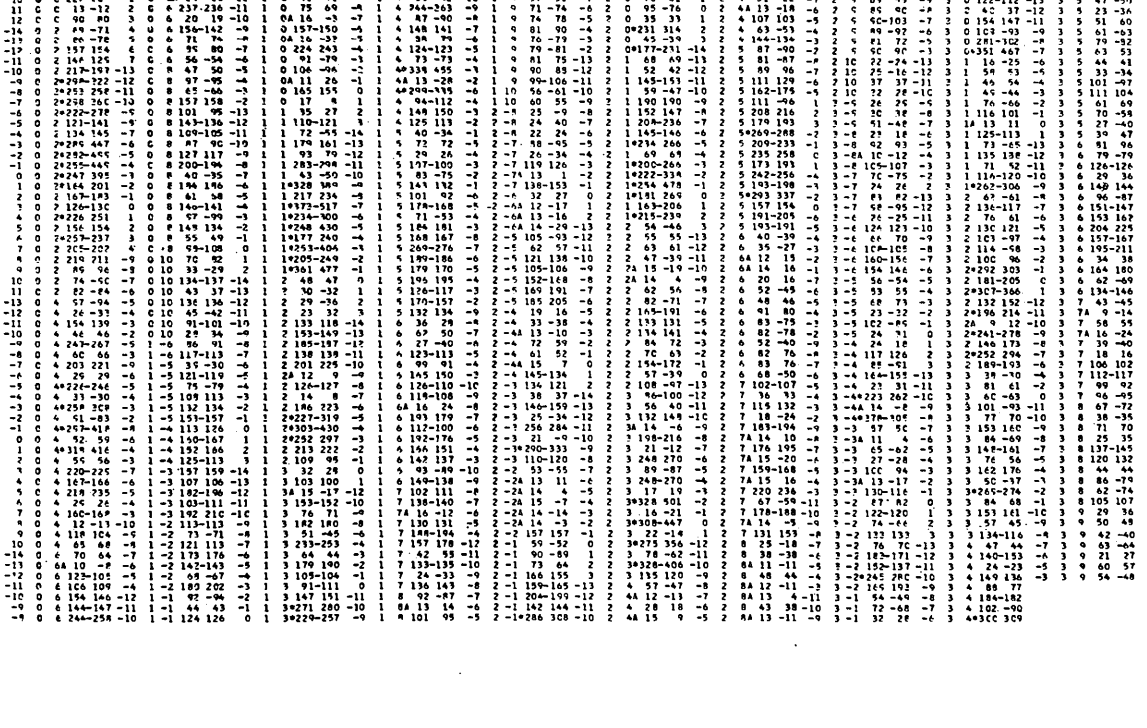

Table 3. *Interatomic distances and bond angles*

AsO_4 tetrahedron	
As–O(1)	1·747 (8) Å
As–O(2)	1·684 (10)
As–O(3)	1·673 (7)
As–O(4)	1·678 (7)
Mean	1·695
O(1)–O(2)	2·623 (11) Å
O(1)–O(3)	2·835 (13)
O(1)–O(4)	2·789 (13)
O(2)–O(3)	2·800 (14)
O(2)–O(4)	2·799 (14)
O(3)–O(4)	2·745 (6)
Mean	2·765
O(1)–As–O(2)	99·7 (0·6)°
O(1)–As–O(3)	112·0 (0·3)
O(1)–As–O(4)	109·0 (0·4)
O(2)–As–O(3)	113·0 (0·4)
O(2)–As–O(4)	112·7 (0·3)
O(3)–As–O(4)	110·0 (0·5)
Mean	109·4°

the AsO_4 tetrahedra also serve as the acceptors of the hydrogen bonds from the two NH_4^+ groups, and thus hold the adjacent chains together.

Table 3 (*cont.*)

O–H···O bond	
$O(1^{i})$–$O(4^{iii})$*	2·669 (13) Å
NH_4 group (1)	
N(1)–H···$O(2^{iii})$	2·781 (13) Å
N(1)–H···$O(3^{iv})$	2·807 (10)
N(1)–H···$O(3^{ii})$	2·837 (11)
N(1)–H···$O(3^{iii})$	2·925 (17)
N(1)–H···$O(1^{i})$	3·093 (9)
Mean	2·888
$O(2^{iii})$–N(1)–$O(3^{iv})$	99·4 (0·4)°
$O(2^{iii})$–N(1)–$O(3^{ii})$	104·6 (0·5)
$O(2^{iii})$–N(1)–$O(3^{iii})$	118·9 (0·3)
$O(3^{iv})$–N(1)–$O(3^{ii})$	92·4 (0·3)
$O(3^{iv})$–N(1)–$O(3^{iii})$	103·4 (0·4)
$O(3^{ii})$ –N(1)–$O(3^{iii})$	129·8 (0·5)
Mean	108·1°
$O(1^{i})$–N(1)–$O(2^{iii})$	69·1 (0·3)°
$O(1^{i})$–N(1)–$O(3^{iv})$	163·7 (0·4)

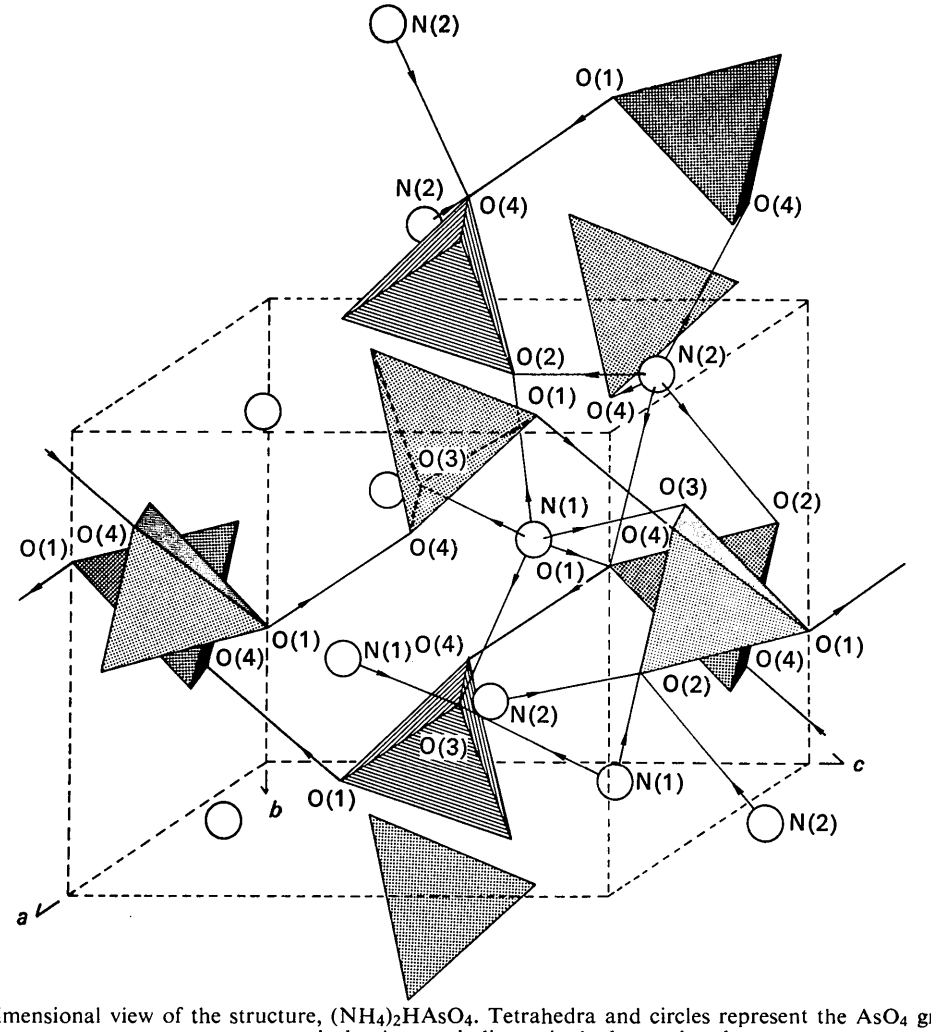

Fig. 1. A three-dimensional view of the structure, $(NH_4)_2HAsO_4$. Tetrahedra and circles represent the AsO_4 groups and the N atoms respectively. Arrows indicate the hydrogen bonds.

Table 3 (*cont.*)

	$O(1^{i})$–N(1)–$O(3^{ii})$	101·6 (0·3)
	$O(1^{i})$–N(1)–$O(3^{iii})$	74·1 (0·4)
NH_4 group (2)		
	N(2)–H···$O(2^{iii})$	2·809 (8) Å
	N(2)–H···$O(4^{iv})$	2·829 (9)
	N(2)–H···$O(4^{i})$	2·864 (15)
	N(2)–H···$O(2^{i})$	2·940 (14)
	N(2)–H···$O(1^{i})$	2·956 (19)
	Mean	2·880
	$O(2^{iii})$–N(2)–$O(4^{iv})$	111·8 (0·3)°
	$O(2^{iii})$–N(2)–$O(4^{i})$	108·4 (0·4)
	$O(2^{iii})$–N(2)–$O(2^{i})$	105·6 (0·3)
	$O(4^{iv})$–N(2)–$O(4^{i})$	113·0 (0·3)
	$O(4^{iv})$–N(2)–$O(2^{i})$	109·8 (0·4)
	$O(4^{i})$—N(2)–$O(2^{i})$	107·9 (0·3)
	Mean	109·4°
	$O(1^{i})$–N(2)–$O(2^{iii})$	70·8 (0·3)°
	$O(1^{i})$–N(2)–$O(4^{iv})$	87·4 (0·4)
	$O(1^{i})$–N(2)–$O(4^{i})$	157·1 (0·3)
	$O(1^{i})$–N(2)–$O(2^{i})$	52·8 (0·3)

* $O(n^{ii})$, $O(n^{iii})$ and $O(n^{iv})$ are obtained from the oxygen atom $O(n^{i})$ at (x,y,z) by the symmetry operations $(\bar{x},\bar{y},\bar{z})$, $(x,\frac{1}{2}-y,\frac{1}{2}+z)$ and $(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$ respectively.

As can be seen, the AsO_4 coordination tetrahedron is not very symmetrical. There are three As–O distances nearly equal with an average value of 1·678 Å, while the fourth distance is equal to 1·747 Å. The tetrahedral angles range from 99·7 to 113·0°. The As–O bond lengths of the AsO_4 group in this structure agree with those found in $Na_2HAsO_4.7H_2O$ (Baur & Khan, 1970). There the three more nearly equal As–O distances have an average value of 1·662 Å and the fourth has value of 1·728 Å. The tetrahedral angles, however, have less dispersion and range between 102·7 and 113·7°. Apparently this is a result of the difference in the atomic bonding in which the AsO_4 groups in the two structures take part. In $(NH_4)_2HAsO_4$, the O(1)–O(2) edge of the AsO_4 group is shared between the neighboring arsenate and ammonium coordination polyhedra. This situation might account for the small value, 99·7, for the O(1)–As–O(2) angle. The average values of the three angles which, respectively, contain and do not contain the long As–O bond are 106·9 and 111·9°, very close to the values found by Baur & Khan (1970) in a discussion of the general shape of the tetrahedral groups in arsenates and phosphates. The O–H · · O bond in this structure has a length of 2·669 Å and can easily be recognized as an unsymmetrical O–H · · O bond (Hamilton & Ibers, 1968). It can be predicted that the hydrogen atom in this O–H · · O bond is attached to the oxygen atom O(1) for which the As–O distance is the largest within the AsO_4 tetrahedron.

There are five oxygen atoms around each of the nitrogen atoms with N · · O distances between 2·781 and 3·093 Å. Four of the oxygen atoms in each case are in a nearly tetrahedral coordination with O–N–O angles ranging between 92·4 and 129·8°. The remainig two N · · O distances, one from N(1) and the other from N(2), are the largest in magnitude among the whole set and connect the two nitrogen atoms to the same oxygen atom O(1). This arrangement of five short N · · O distances, instead of the chemically expected four, around each of the two NH_4^+ ions can be associated with either one of the following three assumptions:

(*a*) The NH_4^+ ions have small rotatory oscillations.
(*b*) The NH_4^+ groups are in static disorder.
(*c*) Each nitrogen atom in addition to three normal N–H · · O bonds also forms one bifurcated bond.

However, it is not possible to differentiate between the three different models from the present results since the positions of the H atoms could not be determined. If the assumption (*c*) above is correct, then the three oxygen atoms O(2), O(3) and O(4), take part in hydrogen bonds as acceptors: O(2) and O(3) three times in the N–H · · O bonds, and O(4) twice in N–H · · O and once in the O–H · · O bond. The situation is slightly different for O(1) which takes part in the O–H · · O bond as a donor and its role in the two weak N–H · · O bonds is that of an acceptor.

Smith, Lehr & Brown (1957) determined the cell constants of $(NH_4)_2HPO_4$ and found the space group to be $P2_1/a$. After transforming the setting, the reported cell constants in space group $P2_1/c$ are as follows: $a=11{\cdot}02$, $b=6{\cdot}68$, $c=8{\cdot}03$ Å; $\beta=113°38'$. The close similarity to the unit-cell data of $(NH_4)_2HAsO_4$ indicates that the two compounds are isomorphous.

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