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The Crystal Structure of Diammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$

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$(NH_4)_2HPO_4$ crystallizes in the space group $P2_1/c$ with cell constants $a=11{\cdot}043$ (6), $b=6{\cdot}700$ (3), $c=8{\cdot}031$ (4) Å, $\beta=113{\cdot}42$ (3)° and $Z=4$, and is isomorphous with $(NH_4)_2HAsO_4$. The structure is refined using three-dimensional data collected on a four-circle automatic diffractometer. The final R value is 0·015 for 649 observed reflections. The positions of the hydrogen atoms indicate that only four among five N···O contact distances (less than 3·2 Å from each NH_4^+ ion) represent the actual N–H···O bonds. The length of the O–H···O bond is 2·615 (1) Å and differs significantly from 2·669 (13) Å found in the isomorphous arsenate. It is suggested that this is a consequence of the size difference between the P^{5+} and As^{5+} ions.

Introduction

In an earlier paper (Khan, Straumanis & James, 1970) the crystal structure of $(NH_4)_2HAsO_4$ is reported. However, it was not possible to determine the positions of the hydrogen atoms during that study and the hydrogen bonding suggested was based only on the contacts between the heavier atoms. Since each NH_4^+ ion in the structure is coordinated by five oxygen atoms, there is a certain amount of ambiguity regarding the N–H···O bonding. The cell dimension data and the space group reported for $(NH_4)_2HPO_4$ by Smith, Lehr & Brown (1957) indicated that this phosphate is isomorphous with the corresponding arsenate. A crystal structure study of $(NH_4)_2HPO_4$ was therefore undertaken to find the actual hydrogen bonding from the NH_4^+ ions by determining the positions of the hydrogen atoms. Further it was deemed desirable to make a comparative study of the two isomorphous sible influence on the structure of a replacement of a P^{5+} ion with an As^{5+} ion.

Experimental

From a commercially supplied crystalline sample of $(NH_4)_2HPO_4$, an almost spherical crystal of diameter 0·40 mm was selected for the X-ray work. The intensity data were collected on a four-circle automatic diffractometer using Ag $K\alpha$ radiation. The details of the experimental procedures are the same as described in some earlier publications (Khan, Baur & Forbes, 1972; Baur & Khan, 1970). Lattice parameters were determined from 12 carefully centered reflections. The intensities were collected in two of the four equivalent quadrants up to $\sin\theta/\lambda=0{\cdot}54$ Å^{-1}. These were averaged after applying the Lorentz–polarization corrections and were converted to F_o values. Absorption corrections were neglected. 1440 non-unique reflecto be zero, which resulted in a total of 649 observed reflections.

Crystal data are: $a=11{\cdot}043$ (6), $b=6{\cdot}700$ (3), $c=8{\cdot}031$ (4) Å, $\beta=113{\cdot}42$ (3)°, $V=545{\cdot}3$ Å³, $Z=4$, $D_x=1{\cdot}608$, $D_m=1{\cdot}619$ g.cm^{-3} (Schiff, 1859), F.W. 131·97. The space group is $P2_1/c$.

The programs were the same as those used by Khan, Baur & Forbes (1972). Atomic scattering factors for P, N, O^- and H were taken from the *International Tables for X-ray Crystallography* (1962).

Starting with the positional parameters for the non-hydrogen atoms as in $(NH_4)_2HAsO_4$ (Khan *et al.*, 1970) the structure was refined by the least-squares method. The refinement converged to a conventional R equal to 0·05, when all the seven atoms were refined anisotropically. A difference Fourier synthesis, at this stage revealed the positions of the nine hydrogen atoms in the structure. The final refinement with isotropic temperature factors for the hydrogen atoms and anisotropic factors for the heavier atoms converged to an R of 0·015. The weighted R is 0·020.

Results and discussion

Positional and anisotropic thermal parameters for the nonhydrogen atoms in $(NH_4)_2HPO_4$ are listed in Table 1 and the root-mean-square thermal displacements for these atoms along the principal axes and their orientations relative to the a, b and c axes are given in Table 2. Positional and isotropic temperature factors for the hydrogen atoms are given in Table 3. Observed and calculated structure factors are compared in Table 4. Fig. 1 shows the structure of $(NH_4)_2HPO_4$ when viewed along the b axis. Table 5 contains selected interatomic bond lengths and bond angles. The structure as described for the isomorphous $(NH_4)_2HAsO_4$ (Khan *et al.*, 1970), consists of PO_4 and NH_4 tetrahedra held together by O–H···O and N–H···O bonds. The interatomic distances and angles have the usual values. Of the four P–O bond lengths within the PO_4 tetrahedron, one is longer than the remaining three, typical of a (PO_3OH) group. The average values of the O–P–O angles which, respectively, contain and do not contain the P–O(1) bond [the P–O(H) bond] are smaller (107·2°) and larger (111·7°) than the ideal tetrahedral angle. The oxygen–oxygen contacts in the PO_4 tetrahedron range between 2·444 and 2·542 Å.

Table 2. $(NH_4)_2HPO_4$ *root-mean-square thermal displacements along principal axes and their orientations relative to* **a**, **b** *and* **c**

	Axis	Displacement	Angle with [100]	[010]	[001]
P	1	0·133 (1) Å	104 (2)°	19 (2)°	73 (2)°
	2	0·145 (1)	135 (7)	91 (4)	111 (7)
	3	0·149 (1)	49 (7)	71 (2)	152 (6)
O(1)	1	0·152 (2)	90 (3)	9 (13)	98 (13)
	2	0·158 (2)	80 (1)	99 (13)	164 (7)
	3	0·229 (2)	10 (1)	88 (1)	103 (1)
O(2)	1	0·146 (2)	90 (2)	30 (2)	63 (2)
	2	0·174 (2)	148 (5)	105 (3)	40 (4)
	3	0·190 (2)	58 (5)	115 (2)	63 (4)
O(3)	1	0·151 (2)	32 (1)	121 (1)	103 (2)
	2	0·193 (2)	94 (3)	110 (5)	146 (5)
	3	0·205 (2)	58 (1)	38 (3)	121 (6)
O(4)	1	0·152 (2)	52 (5)	40 (6)	95 (3)
	2	0·163 (2)	120 (5)	57 (6)	115 (3)
	3	0·184 (2)	127 (3)	71 (3)	25 (3)
N(1)	1	0·159 (3)	22 (7)	107 (9)	99 (4)
	2	0·172 (3)	106 (9)	162 (9)	91 (6)
	3	0·190 (2)	105 (4)	94 (5)	9 (4)
N(2)	1	0·149 (3)	85 (6)	12 (7)	82 (3)
	2	0·165 (2)	147 (6)	80 (7)	98 (6)
	3	0·183 (2)	123 (6)	97 (3)	12 (5)

Table 3. *Positional and isotropic temperature factors for the* H *atoms in* $(NH_4)_2HPO_4$

	x	y	z	B
H(1)	0·179 (2)	0·876 (3)	0·137 (3)	3·1 (5)Å²
H(2)	0·513 (2)	0·160 (2)	0·115 (2)	1·3 (4)
H(3)	0·418 (1)	0·000 (3)	0·115 (2)	1·1 (4)
H(4)	0·496 (2)	0·121 (2)	0·285 (3)	1·8 (4)
H(5)	0·392 (2)	0·205 (3)	0·127 (2)	1·2 (4)
H(6)	0·170 (2)	0·405 (3)	0·186 (2)	1·9 (4)
H(7)	0·125 (1)	0·498 (3)	0·315 (2)	0·5 (3)
H(8)	0·161 (2)	0·292 (3)	0·348 (2)	0·9 (4)
H(9)	0·043 (2)	0·351 (2)	0·197 (2)	0·8 (4)

Each NH_4^+ ion has five N···O contacts which are smaller than 3·4 Å, and the coordination of the oxygen atoms around the N atoms is very similar to that in the isomorphous arsenate. The average values of these N(1)···O and N(2)···O lengths are 2·895 and 2·890 Å respectively in the phosphate. Corresponding values

Table 1. $(NH_4)_2HPO_4$ *positional parameters in fractions of the cell edges and thermal parameters* (×10⁴), *with their standard deviations*

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0·24913 (3)	0·89110 (5)	0·43043 (4)	40 (1)	80 (1)	78 (1)	2 (1)	22 (1)	−4 (1)
O(1)	0·2039 (1)	0·9678 (2)	0·2277 (1)	98 (1)	102 (3)	94 (2)	3 (1)	39 (1)	2 (2)
O(2)	0·2644 (1)	0·0823 (1)	0·5394 (1)	64 (1)	108 (2)	113 (2)	−10 (1)	38 (1)	−23 (2)
O(3)	0·3767 (1)	0·7735 (1)	0·4845 (1)	54 (1)	159 (3)	136 (2)	22 (1)	34 (1)	−1 (2)
O(4)	0·1389 (1)	0·7602 (1)	0·4409 (1)	49 (1)	111 (2)	110 (2)	−7 (1)	23 (1)	5 (2)
N(1)	0·4517 (1)	0·1190 (2)	0·1608 (2)	50 (2)	128 (4)	129 (3)	3 (2)	31 (2)	−1 (3)

Table 4. $(NH_4)_2HPO_4$ *observed and calculated structure factors* (×5)

L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG	L	FO	FC	SIG
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

in the arsenate are 2·888 and 2·880 Å. The angles O···(H–N–H)···O also compare well with those found in the arsenate. Whenever the coordination number of an NH_4^+ ion in crystal structures is higher than 4, it is difficult to postulate a correct N–H···O bonding from the positions of N and O atoms alone. The difficulty increases with the increase in the coordination number. In the isomorphous structures of $(NH_4)_2HPO_4$ and $(NH_4)_2HAsO_4$, the first four N···O contacts around each of the two NH_4^+ ions have nearly tetrahedral values for the O–N–O angles and therefore represent the N–H···O bonds. The hydrogen positions determined in $(NH_4)_2HPO_4$ confirm this conclusion (Table 5). However, the fifth N···O contact, smaller than 3·2 Å for each NH_4^+ ion, was thought to be a result of dynamic or static disorder of the ammonium ion or that each N atom in addition to three normal N–H···O bonds also formed one bifurcated bond (Khan *et al.*, 1970). The average value of the electron density at the H atom positions in $(NH_4)_2HPO_4$ is 0·63 Å^{-3} which, according to our experience, is the normal value for the H atom peaks in other structures investigated by the X-ray method. The isotropic temperature factors for the H atoms belonging to the NH_4^+ groups are not large and have an average value of 1·2 Å^2. These considerations do not favor a model in which the NH_4^+ ions are in a state of disorder (dynamic or static).

At the same time there is not enough evidence to suggest that the short N(1)···O(1) or N(2)···O(1) distances are a result of bifurcated bonding. The shortest contact which the oxygen atom O(1) has with any H atom of the NH_4^+ group is 2·50 Å from H(8). The angle N(2)–H(8)···O(1) is 114 (1)°. On the other hand the hydrogen bonding suggested in Table 5 involves normal H···O contacts and the angles N–H···O are also large, indicating that the N–H···O bonds are more or less linear, and this is particularly true for the bonds from the N(2) atom. This conclusion is also supported on the basis of the electrostatic bond-strength considerations. The bond strengths received by the oxygen atoms O(1), O(2), O(3) and O(4) are respectively 2·08, 1·75, 1·75, 1·75 v.u. The oxygen atom O(1) which acts as a donor in the only O–H···O bond in the structure, is saturated and is not well qualified to act as an acceptor of a hydrogen bond.

It was pointed out earlier (Khan & Baur, 1972) that like other cations, the effective radius of the NH_4^+ ion increases with an increase in coordination number (C.N.). The NH_4^+ ion can, in some crystal structures, replace an alkali atom of comparable size, such as K^+, Rb^+ or Cs^+. Nevertheless the ammonium ions in these structures tends to have a smaller C.N. than the replaced alkali atom and thus exhibits a tendency to engage in N–H···O bonding. It is not surprising,

Table 5. *Interatomic bond distances, bond angles and hydrogen bonding in* $(NH_4)_2HPO_4$

(*a*) PO_4 tetrahedron

P–O(1)	1·587 (1) Å
P–O(2)	1·522 (1)
P–O(3)	1·519 (1)
P–O(4)	1·530 (1)
Mean	1·539
O(1)–P–O(2)	103·61 (6)°
O(1)–P–O(3)	109·84 (5)
O(1)–P–O(4)	108·01 (5)
O(2)–P–O(3)	113·19 (5)
O(2)–P–O(4)	111·07 (5)
O(3)–P–O(4)	110·77 (5)
O(1)–O(2)	2·444 (2) Å
O(1)–O(3)	2·542 (2)
O(1)–O(4)	2·522 (2)
O(2)–O(3)	2·539 (2)
O(2)–O(4)	2·516 (2)
O(3)–O(4)	2·509 (2)

(*b*) O–H···O bonding

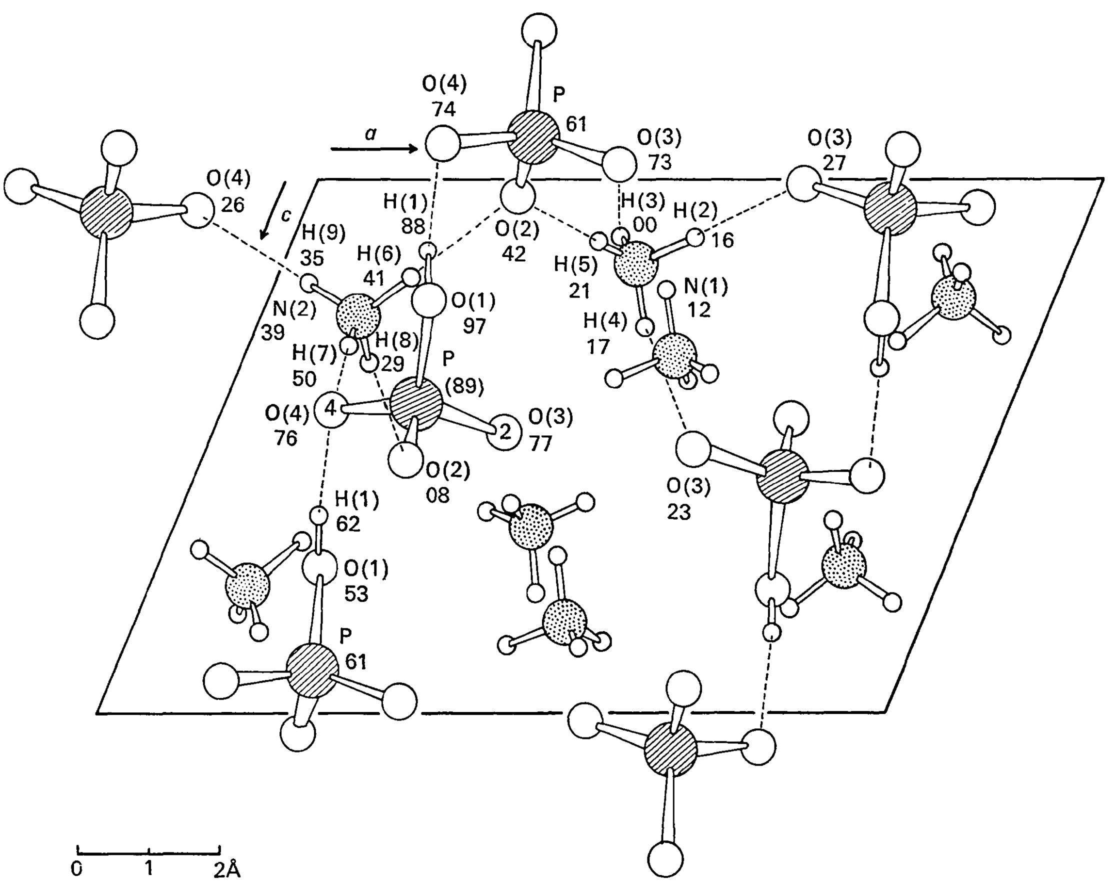
O(1)–H(1)···O(4)=2·615 (1) Å
O(1)–H(1)=0·91 (2) Å

Table 5 *(cont.)*

(*c*) N–H···O bonding

	N–H	H···O	N–H···O/N···O	∠N–H···O
N(1)–H(2)···O(3)	0·93 (1) Å	1·87 (1) Å	2·789 (1) Å	172 (1)°
N(1)–H(3)···O(3)	0·89 (2)	2·07 (2)	2·946 (2)	166 (1)
N(1)–H(4)···O(3)	0·92 (2)	1·96 (2)	2·817 (2)	154 (1)
N(1)–H(5)···O(2)	0·84 (2)	1·93 (2)	2·763 (2)	175 (2)
N(1)········O(1)	–	–	3·158 (1)	–
N(2)–H(6)—O(2)	0·96 (1)	1·86 (1)	2·822 (1)	175 (2)
N(2)–H(7)—O(4)	0·86 (2)	2·00 (2)	2·860 (2)	178 (1)
N(2)–H(8)—O(2)	0·91 (2)	2·06 (2)	2·965 (2)	175 (1)
N(2)–H(9)—O(4)	0·85 (1)	1·96 (1)	2·814 (1)	176 (2)
N(2)————O(1)	–	–	2·989 (2)	–

	∠H–N–H	∠O···(HNH)···O
O(3)···H(2)–N(1)–H(3)···O(3)	110 (1)°	103·80 (5)°
O(3)···H(2)–N(1)–H(4)···O(3)	106 (1)	91·84 (4)
O(3)···H(2)–N(1)–H(5)···O(2)	106 (1)	96·98 (5)
O(3)···H(3)–N(1)–H(4)···O(3)	115 (2)	131·46 (6)
O(3)···H(3)–N(1)–H(5)···O(2)	110 (2)	116·68 (5)
O(3)···H(4)–N(1)–H(5)···O(2)	111 (1)	106·28 (5)
O(2)···H(6)–N(2)–H(7)···O(4)	105 (1)	108·00 (5)
O(2)···H(6)–N(2)–H(8)···O(2)	111 (1)	105·32 (4)
O(2)···H(6)–N(2)–H(9)···O(4)	110 (1)	110·84 (5)
O(4)···H(7)–N(2)–H(8)···O(2)	108 (2)	108·34 (5)
O(4)···H(7)–N(2)–H(9)···O(4)	112 (1)	113·68 (4)
O(2)···H(8)–N(2)–H(9)···O(4)	110 (1)	110·28 (5)



therefore, that in $(NH_4)_2HPO_4$-type structures, the NH_4 groups (C.N.=5) form normal N–H···O bonds. The average N–H length is 0·90 Å and compares well with the values determined by X-ray methods. For example, it is 0·93 Å in $(NH_4)_3PO_4$ (Mootz & Wunderlich, 1970). The tetrahedral angles H–N–H in $(NH_4)_2HPO_4$ do not show a severe distortion of the NH_4^+ groups.

A significant difference which exists in the isomorphous structures of $(NH_4)_2HPO_4$ and $(NH_4)_2HAsO_4$ is in the length of the hydrogen bond O(1)–H(1)···O(4). This bond is shorter in the phosphate, 2·615 (1) Å, than in the arsenate, 2·669 (13) Å and the difference is nearly four times the combined errors. If the electronegativity (2·1 for P and 2·0 for As) or the size (ionic radius for P^{5+}=0·35 and for As^{5+}=0·47 Å) of an X atom in HXO_4 groups (X=P or As) can influence the length of a O–H···O bond, it is likely that the bonds from the OH groups will be influenced more than the O–H···O bonds from any H_2O molecule present in the structure. Two pairs of isomorphous phosphates and arsenates containing OH groups have been studied carefully by the X-ray method: $Na_2HPO_4.7H_2O$ and $Na_2HAsO_4.7H_2O$ (Baur & Khan, 1970) and $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ (Khan & Baur, unpublished work). The O–H···O bond lengths in these four structures, given in the same order as above, are 2·658 (8), 2·662 (5), 2·490 (2) and 2·517 (3) Å and indicate that the O–H···O bond lengths in phosphates are either equal or slightly shorter than in the isomorphous arsenates. Unlike these structures where the oxygen atoms of the (OH) groups take part in more than one hydrogen bond by also accepting bonds either from (H_2O) molecules or from NH_4^+ ions, in $(NH_4)_2HPO_4$ or in $(NH_4)_2HAsO_4$, the oxygen atom O(1) of the OH group is involved in only one O–H···O bond. There is, therefore, some reason to expect that the O–H···O bond in this isomorphous pair of structures will be influenced most when P^{5+} is replaced by As^{5+}. Baur (1970) has observed an inverse relation between the O–H···O bond length and the difference, Δp, in the bond strengths received by the donor and the acceptor atoms: $\Delta p = p_{donor} - p_{acceptor}$, where p_{donor} and $p_{acceptor}$ represent the bond strengths received by the donor and the acceptor atoms. According to this relation a shorter O–H···O bond in the phosphate indicates an increase in Δp. Assuming that the bond strength is also a function of the interionic distance in addition to the charge and coordination number, the observed difference may be explained as a consequence of an increase in p_{donor} due to closer proximity of the donor atom to the P^{5+} ion than to the As^{5+} ion. Since in this structure the bonds link one PO_4^{3-} (or AsO_4^{3-}) group to another it has been implied here that the changes in p_{donor} have more pronounced effect on the O–H···O bond lengths than the changes in the $p_{acceptor}$.

Every atom in the structure (not considering the hydrogen atoms) displays the anisotropic character of the thermal vibrations. The anisotropy is minimum for the P atom and maximum for the O(1) atom (Table 2). The major component of the maximum r.m.s. thermal displacement of the O(1) atom is along the *a* axis and in a direction perpendicular to the O–H···O bonds.

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