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A Neutron Structure Analysis of Tetragonal $NH_4H_2PO_4$*

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The structure of tetragonal $NH_4H_2PO_4$ has been determined in a single-crystal neutron-diffraction study. The N–H · · · O and O–H · · · O bond systems suggested in earlier X-ray investigations were confirmed. The $H_2PO_4^-$ network is very similar to that found in KH_2PO_4; the only significant difference observed was in the angle between the P–O and O–H · · · O bonds. The ammonium ion was found to be only slightly distorted from a regular tetrahedral arrangement. Considerable distortion would be necessary for linear N–H · · · O bonds. The observed angle between the N–H bond and the line joining nitrogen and oxygen centers was about 14°. In order to achieve good agreement between calculated and observed data it was necessary to introduce anisotropic thermal vibration parameters. The final value of the discrepancy factor was 8·9%.

1. Introduction

Ammonium dihydrogen phosphate (commonly designated ADP) is a member of an isomorphous series of phosphates and arsenates that are of interest in crystal physics because of their strong piezoelectric activity and their low-temperature transitions. In all but the ammonium salts, the transitions are to ferroelectric phases; the ammonium salts apparently become antiferroelectric. In order to understand the special role of the ammonium ion in these compounds, one must first look to a detailed comparison of the crystal structures of typical members of the series. The structures of KDP (KH_2PO_4) and ADP are convenient ones for such a comparison.

The structures of KDP on either side of the ferroelectric Curie point have been studied in detail by both X-rays and neutrons (West, 1930; Frazer & Pepinsky, 1953; Peterson, Levy & Simonsen, 1953; Bacon & Pease, 1953, 1955; Levy, Peterson & Simonsen, 1954; Pease & Bacon, 1954). Similar X-ray analyses have been made for ADP (Ueda, 1948; Frazer, 1948; Keeling & Pepinsky, 1955); but prior to the investigation reported here, neither of the two ADP structures had been examined by neutrons. The importance of neutrons, of course, lies in the determination of accurate hydrogen positions. Since there is abundant evidence that the hydrogens play a very significant role in the transition, their location is of essential importance to the problem.

In the present investigation, the room-temperature tetragonal structure has been determined in a single-crystal neutron-diffraction study. While a complete understanding of the structural nature of the transition, and its relationship to that of KDP, must await neutron examination of the low-temperature orthorhombic phase, the results obtained provide a necessary first step in the analysis.

2. Experimental

The crystal used was a $3\times2\times10$ mm.^{3} pillar (cut from a commercial piezoelectric *c* plate). The *c* axis was along the smallest dimension and the *a* axes along the other two. The pillar was dipped several times in liquid nitrogen to minimize extinction effects. Because of the low-temperature transition, which always shatters an ADP crystal of such size, the sample was altered into a translucent mass of adhering oriented fragments. The fragments held together sufficiently well, however, to permit careful handling. The sample was dipped in a solution of Duco cement and acetone for strengthening, and then mounted with its long dimension (along an *a* axis) parallel to the diffractometer axis of rotation. This *a*-axis mounting was chosen because the $\overline{4}$ symmetry of ADP permits one to measure all of the atomic coordinates from a single projection on (100).

Crystal and counter settings were calculated for a mean neutron wavelength of 1·063 Å and ADP cell dimensions:

$$a = b = 7{\cdot}502,\quad c = 7{\cdot}546\ \text{Å}\,.$$

The latter were obtained by averaging the various

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observations of several earlier investigators (see Table 1).

Table 1. *Cell dimensions reported for* ADP

$a = b$	c	Reference
7·48 Å	7·56 Å	Hassel, 1925
7·51	7·53	Hendricks, 1927
7·53	7·542	Mason, 1946
7·479	7·516	Ueda, 1948
7·50	7·58	Frazer, 1948
7·514	7·546	Jaffe, 1949
7·502	7·546	Mean values adopted here

Sixty-four non-equivalent ($0kl$) reflections were recorded, the smallest interplanar spacing being $d(0,4,12) = 0{\cdot}594$ Å. Effects of second-order contamination were small, but corrections were made for them. Absorption and extinction effects were negligibly small.

3. The first trial structure

As determined in the earlier X-ray studies, the tetragonal phase of ADP belongs to the space group $I\bar{4}2d$. There are four $NH_4H_2PO_4$ formula units per cell. Phosphorus positions are at $(0, 0, 0)$, $(\frac{1}{2}, 0, \frac{1}{4})$ and at similar points about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; nitrogen positions are at $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{3}{4})$ and at similar points about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The hydrogens H_N of the ammonium group and the oxygens occupy 16-fold general positions (x, y, z). For the H_O hydrogens in the O–H $\cdots$ O system, one would ordinarily choose the 8-fold (d) position, which would put a proton midway between the oxygens on each hydrogen bond joining adjacent PO_4 groups. However, in the case of KDP, Bacon & Pease (1953) demonstrated that one could not distinguish between a strongly anisotropic oscillation of the proton about this position and a model involving random distribution of protons on 16-fold general positions, each effectively populated by a half-proton. Since the earlier X-ray results on ADP indicated an O–H $\cdots$ O bond length very nearly the same as in KDP, it was expected that a similar ambiguity would be encountered in the present work. The low-temperature ordering in KDP and certain other considerations suggest strongly that the half-proton model is the correct one. Accordingly, this model was selected for trial calculations.

The first trial structure was constructed on the following assumptions:

(i) Oxygen coordinates were chosen by averaging the X-ray values reported by Ueda (1948) and Frazer (1948).

(ii) H_N positions were calculated by assuming a regular NH_4^+ tetrahedron with an N–H separation of 1·03 Å (NH_4Cl, Levy & Peterson, 1952) and so oriented as to conform to the N–H $\cdots$ O bond system postulated on the basis of interatomic distances in the X-ray studies.

(iii) In deriving trial H_O positions, half-protons were assumed to occupy double potential minima on the O–O line of centers, with a shortest O–H distance of 1·04 Å.

(iv) Approximate isotropic temperature parameters were estimated for each atom by studying the available data on ADP, KDP, and NH_4Cl.

The resulting trial parameters are collected in Table 2.

Table 2. *Parameters for first trial structure*

Atom	x	y	z	B
P	0	0	0	$0{\cdot}98 \times 10^{-16}$ cm.^{2}
N	0	0	$\frac{1}{2}$	1·84
O	0·083	0·151	0·124	1·21
H_N	0·026	0·109	0·579	2·50
H_O	0·222	0·151	0·125	2·21

The neutron-scattering lengths used in structure-factor calculations, and in all subsequent calculations, were taken from the compilation of Shull & Wollan (1956), and had the following values:

$$b_P = 0{\cdot}530,\quad b_N = 0{\cdot}940,\quad b_O = 0{\cdot}580,\quad b_H = -0{\cdot}378$$

(all in units of 10^{-12} cm.).

The discrepancy factor $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ for this first trial structure was 0·19.

4. Refinement of the structure

Starting with the trial parameters in Table 2, several Fourier refinement cycles were computed on X-RAC, using the backshift method and difference syntheses. The difference syntheses were of two types. One employed the conventional Fourier coefficients (F_o-F_c). The other was of the type computed by Bacon &

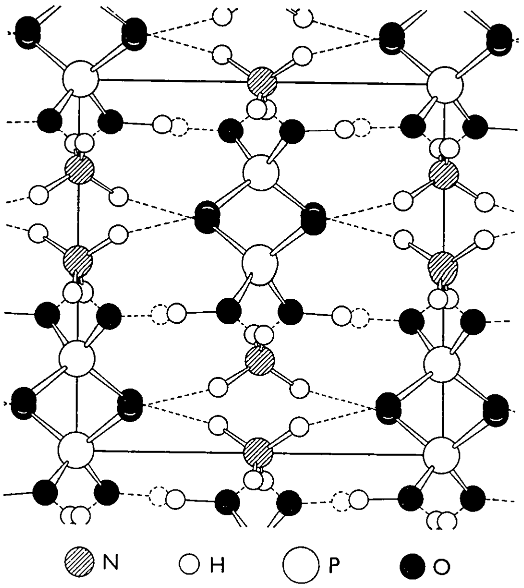

Fig. 1. The (100) projection of the $NH_4H_2PO_4$ structure.

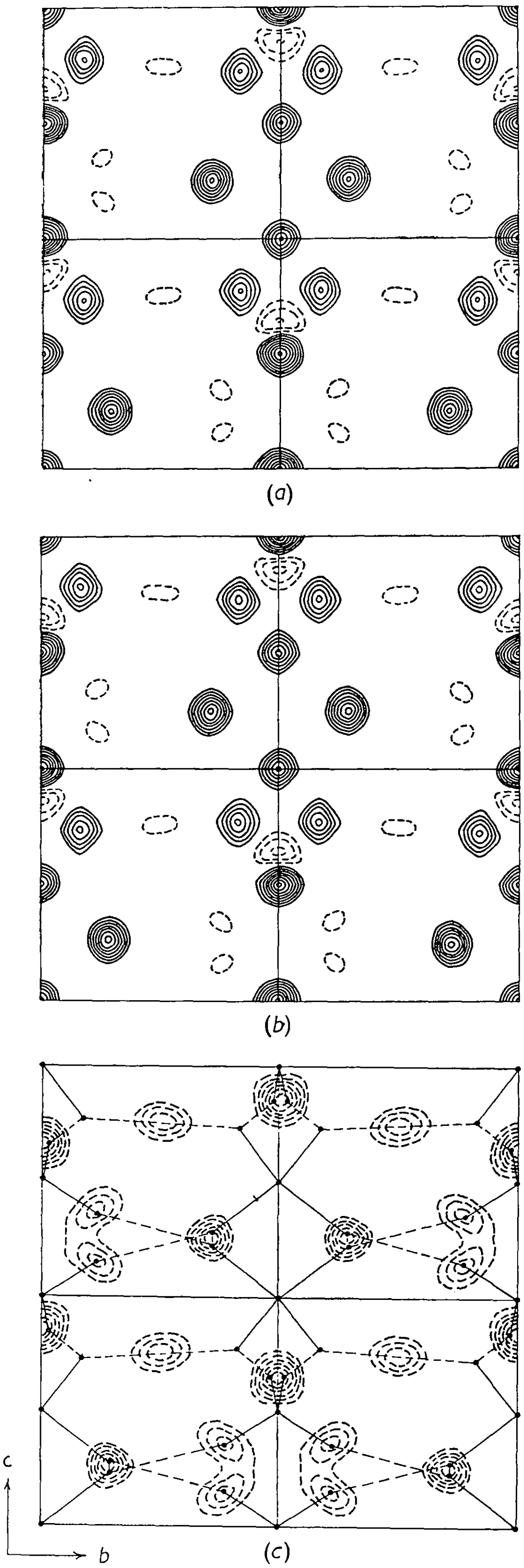

Fig. 2. (*a*) Observed neutron data in Fourier projection of ADP structure on (100) (X-RAC tracing). (*b*) Calculated neutron data in Fourier projection of ADP structure on (100) (X-RAC tracing). (*c*) Hydrogen peaks obtained using (F_o-F_c') Fourier coefficients (X-RAC tracing).

Pease in their studies of KDP, and involved coefficients (F_o-F_c'), where F_c' represents a calculated structure factor from which the hydrogen contributions have been omitted. One thus obtains an 'observed' hydrogen-only map. In all of the structure factor and Fourier calculations the origin was shifted to $(0, 0, \frac{1}{8})$ in order to make use of a center of symmetry in the projection on (100).

It soon became apparent that anisotropic temperature factors would be necessary for further improvement of the structure. An isotropic correction appeared to be adequate for nitrogen, and the H_O hydrogens were being taken care of satisfactorily by isotropic corrections on the half-proton model, but anisotropic vibrations were clearly in evidence for the remaining atoms. The case of phosphorus could be dealt with easily, since symmetry prescribes that a vibrational ellipsoid for this atom be one of revolution with its axis parallel to *c*. General orientations are permitted for the oxygens and H_N hydrogens, however. As a consequence of symmetry, the ellipsoidal density for these atoms will be seen in four orientations when viewed in projection on (100). There are, of course, certain relationships between these orientations. If the temperature factor for one of them is written in the form

$$T_1 = \exp\,[-\beta_{22}k^2+\beta_{33}l^2+\beta_{23}kl)]\,,$$

then the parameters appropriate to the other three can be selected from Table 3. The *c* component of vibration must be the same for each orientation. Also, the ellipses in the projection are related in mirror-image pairs. The coordinate set assignment in Table 3 is that actually used for both oxygen and hydrogen.

Table 3. *Anisotropic temperature parameters for general positions*

Orientation	Coordinate set	Temperature factors		
1	$\bar{y}, x, \bar{z};\ \frac{1}{2}-y, \bar{x}, \frac{1}{4}+z$	β_{22}	β_{33}	β_{23}
2	$y, \bar{x}, \bar{z};\ \frac{1}{2}+y, x, \frac{1}{4}+z$	β_{22}	β_{33}	$-\beta_{23}$
3	$\bar{x}, \bar{y}, z;\ \frac{1}{2}-x, y, \frac{1}{4}+z$	β_{11}	β_{33}	β_{13}
4	$x, y, z;\ \frac{1}{2}+x, \bar{y}, \frac{1}{4}-z$	β_{11}	β_{33}	$-\beta_{13}$

Table 4. *Summary of final parameters*

	P	N	O	H_N	H_O
x	0	0	0·085	0·014	0·227
y	0	0	0·146	0·111	0·146
z	0	$\frac{1}{2}$	0·115	0·573	0·122
β_{11}	0·00373	0·00830	0·00628	0·01688	0·00927
β_{22}	0·00373	0·00830	0·00594	0·01335	0·00927
β_{33}	0·00470	0·00830	0·00801	0·01669	0·00927
β_{13}	0	0	0·00216	0·00707	0
β_{23}	0	0	0·00124	0·00062	0

Table 5. *Comparison of observed and calculated structure factors*

h	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_c
0	0	4	1·29	−1·14			4	3·84	−3·48			12	3·30	−3·35			9	<0·4	0·33
		8	8·18	8·80			6	3·64	−3·65	0	5	1	2·28	−2·52	0	8	2	3·07	2·91
		12	0·85	−0·46			8	5·96	6·17			3	0·80	−1·30			4	3·99	−4·22
0	2	0	5·19	5·19			10	1·83	−2·03			5	<0·3	0·51			6	2·71	2·19
	4		1·07	−0·71			12	1·24	−1·14			7	<0·4	0·33			8	2·88	2·86
	6		2·60	2·68	0	3	1	4·20	−4·15			9	1·26	−0·93	0	9	1	<0·4	−0·07
	8		1·81	1·55	0	3	3	3·30	−3·96			11	1·02	1·35			3	1·20	−0·84
	10		2·35	1·93			5	0·79	0·43	0	6	2	6·62	6·59			5	<0·4	0·13
	12		4·70	4·33			7	2·26	−2·45			4	4·94	−5·18			7	1·18	−1·08
0	1	1	4·00	4·05			9	1·42	−1·01			6	3·40	3·03	0	10	2	3·13	−3·23
		3	1·39	1·07			11	<0·4	−0·34			8	2·45	2·62			4	3·26	−3·29
		5	5·26	5·44	0	4	2	3·79	4·11			10	1·18	1·18			6	2·23	−2·39
		7	2·05	−2·15			4	−9·48	−9·82	0	7	1	2·28	2·32	0	11	1	0·79	−1·00
		9	0·79	1·16			6	−0·62	−0·43			3	2·00	2·14			3	1·63	−1·80
		11	0·52	−0·38			8	0·44	0·33			5	1·99	2·25			5	<0·4	−0·21
0	2	2	2·91	−2·53			10	0·98	−0·57			7	0·92	1·33	0	12	2	1·62	−1·70

From a difference map it was possible to obtain fairly good estimates for the axial orientations of the ellipses and the root-mean-square displacements along the axes. From these data the various β values were calculated, and then successive difference-map refinements dropped the discrepancy factor to 0·089. While general least-squares calculations would probably have resulted in even better agreement, it was then considered that the principal objectives of the investigation had been attained. The final parameters are summarized in Table 4 and a schematic projection of the structure is shown in Fig. 1. The final Fourier maps are shown in Fig. 2. Calculated and observed structure factors are compared in Table 5.

5. Discussion of results

In so far as the results of this investigation can be compared with the earlier X-ray results, they show much better agreement with the 153 °K. structure of Keeling & Pepinsky than with the older room-temperature studies of Ueda and Frazer. Keeling & Pepinsky seem to have used somewhat more careful experimental procedure than that described in the other two papers, and also these investigators made corrections for termination-of-series errors (by difference maps) whereas such techniques were undeveloped at the time of the older studies. A comparison of oxygen parameters is shown in Table 6.

Table 6. *Comparison of oxygen parameters*

	Present paper	Keeling & Pepinsky	Ueda	Frazer
x	0·085	0·083	0·083	0·083
y	0·146	0·147	0·148	0·154
z	0·115	0·115	0·125	0·122

In comparing their low-temperature structure with the two room-temperature determinations, Keeling & Pepinsky ascribed the differences to genuine temperature effects. Particular attention was called to a 'contraction' of the P–O distance. For this distance Frazer and Ueda had obtained 1·61 Å and 1·58 Å respectively, whereas the distance reported by Keeling & Pepinsky was 1·50 Å. This last value appears to be a typographical error, since a check calculation shows it to be 1·53 Å. Even so, this would imply a sizable change with temperature, if the earlier values could be relied upon. The present study suggests that the results of the earlier studies were not sufficiently accurate for valid comparison at different temperatures. As shown in Table 7, the P–O distance obtained in the present paper is so close to that of Keeling & Pepinsky that it is doubtful if any contraction takes place. There is perhaps some possibility of variation with temperature in the case of the N–H ··· O bond length.

Table 7. *Interatomic distances and bond angles*

	Present paper	Keeling & Pepinsky	Bacon & Pease (KDP room temp.)
P–O	$1{\cdot}53_6$ Å	1·53 Å	1·538 Å
O–O	$2{\cdot}53_6$ Å	2·52 Å	2·528 Å
O–O′	$2{\cdot}49_5$ Å	2·49 Å	2·503 Å
O–P–O	111° 12′	111° 02′	110° 34′
O–P–O′	108° 37′	108° 42′	108° 45′
O–H_O ··· O	$2{\cdot}48_0$ Å	2·50 Å	2·487 Å
O–H_O	1·07 Å	—	1·07 Å
H_O–H_O	0·35 Å	—	0·35 Å
P–O–H_O	116° 17′	—	113° 15′
P–O(H_O)–O	116° 42′	116° 05′	113° 15′
N–H_N	$1{\cdot}00_4$ Å	—	—
H_N–H_N	$1{\cdot}67_9$ Å	—	—
H_N–H'_N	$1{\cdot}61_9$ Å	—	—
H_N–N–H_N	113° 26′	—	—
H_N–N–H'_N	107° 31′	—	—
N–O	$3{\cdot}17_0$ Å	3·16 Å	—
N–H_N ··· O	$2{\cdot}91_5$ Å	2·88 Å	—
H_N–N–O	14° 01′	—	—
H_N–O (bonded)	$1{\cdot}95_6$ Å	—	—
H_N–O (unbonded)	$2{\cdot}65_0$ Å	—	—

The primed atoms in the table are at opposite *z* elevations (relative to the central atom of the tetrahedral arrangement) from those of the unprimed. The H_O–H_O distance refers to the separation between the two half-proton positions on the O–H ··· O bond. The N–H ··· O distance in the table is not the sum of the distances from hydrogen to nitrogen and to oxygen, but is the distance from nitrogen to oxygen. (The hydrogen is not on the line joining these two atoms.) The N–O distance in the table refers to the set of four oxygens that are not hydrogen-bonded with the ammonium group. (Each oxygen atom *is* hydrogen-bonded to *some* ammonium group, but a particular ammonium group is surrounded by eight oxygen neighbors, four of which are linked to the group by hydrogen bonds.)

Table 7 also gives a comparison (where possible) between the ADP results and those obtained by Bacon & Pease in their room-temperature neutron study of KDP. One finds a remarkable similarity in the H_2PO_4 systems in the two crystals. The only significant difference occurs in the angle between the P–O bond and O–H $\cdots$ O bond. This one might expect from differences in *c*-direction packing (compare cell dimensions: $a = 7{\cdot}502$ Å, $c = 7{\cdot}546$ Å for ADP, and $a = 7{\cdot}434$ Å, $c = 6{\cdot}945$ Å for KDP). However, it would seem from the difference in ADP between this bond angle and the angle between P–O and O–H that the structure 'wants' to assume an angle more nearly equal to that observed in KDP, but is prevented from doing so by the size and shape of the ammonium ion.

The tetrahedral ammonium ion is found to be slightly distorted, presumably as a result of hydrogen bonding with neighboring PO_4-groups. The distortion is not so great, however, as to result in linear N–H $\cdots$ O bonds. The N–H bond is about 14° off the line joining nitrogen and oxygen centers.

The temperature parameters were excluded from the comparison in Table 7, since these quantities would not be expected to compare closely in the three studies. If one analyses the temperature parameters given in Table 4, it appears that the oxygens and the ammonium hydrogens both have their major vibration axes in planes $x = k_j y$, where the constant k_j equals x_j/y_j (the ratio of the coordinates of the *j*th atom). In the case of H_N the major vibration axis is approximately perpendicular to the N–H bond. In the case of oxygen the major vibration axis is tilted from the vertical (*c* direction) by about 30°, the tilt being such as to approach being transverse to the P–O bond.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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On the adoption of standard symbols for the settings of single-crystal diffractometers.

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The settings of three-circle single-crystal diffractometers when used as 'cone diffractometers' (Furnas & Harker, 1955) are simply the spherical polar co-ordinates of the reciprocal lattice points with θ, the Bragg angle, given by the radial co-ordinate $2 \sin \theta$. It seems desirable, therefore, that the symbols used to identify the diffractometer circles should be those used for reciprocal-lattice co-ordinates. For this reason the notation adopted in our paper on the determination of diffractometer settings (Arndt & Phillips, 1957) was based on Bernal's