The Crystal Structure of Dipotassium Ethyl Phosphate Tetrahydrate
$K_2(C_2H_5)PO_4.4H_2O$: A Problem in Pseudo-symmetry

By W. S. McDonald* and D. W. J. Cruickshank†

Chemistry Department, University of Glasgow, Glasgow W.2, Scotland

The structure is pseudo-symmetric with super-group *Bmab*. A small number of weak reflexions show the true space group to be *Pccn*. An attempt was made to determine the deviations from pseudo-symmetry by using both the weak and strong reflexions. The final residual was 11·9%, but it was not possible to determine reliably all the parameters of the true structure. The bond lengths in the ethyl phosphate ion are P–O = 1·52 ± 0·02, P–O (ethyl) = 1·56 ± 0·02, C–O = 1·47 ± 0·03, and C–C = 1·53 ± 0·04 Å.

Introduction

The need for an accurate analysis of a structure containing the $(PO_3.OR)^{2-}$ ion was pointed out by Cruickshank (1961) in his discussion of π-bonding in phosphate ions. On the basis of expected π-bond orders, a length of 1·62–1·63 Å was predicted for the P–O(R) bond. The present analysis was undertaken in the hope of obtaining accurate dimensions for the ethyl phosphate anion. In the event the analysis was complicated by serious pseudo-symmetry, which we were able to resolve fairly completely. Though we were not entirely successful, an account of our methods may be helpful to others facing similar but less extreme problems. [See also the successful solution of the pseudo-symmetric structure of potassium niobate by Katz & Megaw (1967)].

Preparation of crystals

A sample of $K_2EtPO_4.H_2O$ was kindly supplied by Dr Maryon Dougill. This material was obtained by drying at 100°C the product which crystallized from water, but it was not suitable for single-crystal work. A saturated aqueous solution of the salt was evaporated at room temperature over KOH pellets in a desiccator. Large, irregular deliquescent crystals were obtained. For the X-ray measurements small fragments of these crystals were removed from the solution and sealed in capillaries.

Space group and cell dimensions

From Weissenberg and precession photographs the crystals were seen to be orthorhombic, with systematic absences as follows:

hkl:	$h+l$ odd,
$h0l$:	h odd, l odd,
$hk0$:	h odd, k odd,
$0kl$:	l odd.

* Present address: School of Chemistry, University of Leeds, Leeds, LS2 9JT, England.
† Present address: Chemistry Department, University of Manchester Institute of Science and Technology, Manchester, M60 1QD, England.

The space group is thus $B2cb$ (no. 41) or $Bmab$ (no. 64). The cell dimensions, measured from zero-layer precession photographs, are $a = 10·03 \pm 0·01$, $b = 20·65 \pm 0·02$, $c = 10·47 \pm 0·01$ Å. The density, determined by flotation in a CCl_4–CH_2I_2 mixture, is 1·67. Eight formula units of $K_2EtPO_4.4H_2O$ per cell give a calculated density of 1·680. The crystals were therefore those of a tetrahydrate.

A long-exposure rotation photograph, taken with the crystal rotating about the [101] axis, showed some weak reflexions on the $h+l$ odd rows, indicating that the B face centring is imperfect, and that the true lattice is primitive. As these extra reflexions are extremely weak, they were ignored in the first stages of the structure determination, and the structure was treated as if it had a B lattice.

Solution of the structure in space group *Bmab*

Equi-inclination Weissenberg photographs were taken with the crystal oscillated about the [101] axis. Cu $K\alpha$ radiation was used, and multiple film photographs of layers $h+l = 0$, 2, 4 and 6 were obtained. Intensities were estimated visually and corrected for Lorentz and polarization factors with a computer program written by J. G. Sime. 624 independent structure amplitudes were measured. For the solution of the structure these were put on a single scale by means of the 134 reflexions observed on more than one layer.

A sharpened three-dimensional Patterson synthesis showed that the potassium and phosphorus atoms were in special positions of the centrosymmetric space group *Bmab*. Two successive Fourier syntheses revealed the positions of the oxygen and carbon atoms, also consistent with space group *Bmab*, and led to an R value of 0·18.

Least-squares refinement was carried out using the KDF9 program of J. G. F. Smith and D. W. J. Cruickshank. The full set of 758 independently observed structure factors was used, with refinement of separate scale factors for the four Weissenberg layers. The weighting scheme was

$$w = 1/(20 + |F_o| + 0·006 |F_o|^2).$$

Refinement of atomic coordinates and isotropic temperature factors reduced the residual to 13·5%. Allowance for anisotropic vibrations further reduced R to 10·7%, and gave the parameters shown in Table 1. All of the atoms in special positions on the mirror plane ($x=0$) are seen to have their largest vibrations normal to the plane.

Determination of the true space group

Since the $h+l$ odd reflexions are extremely weak, and the refinement assuming space group $Bmab$ led to a relatively low R value, the displacements of the true structure from the $Bmab$ structure cannot be very great. The full symmetry elements of this space group are

$$(B, 2+2_1/m+c, 2_1+2_1/a+c, 2+2_1/b+n).$$

The weak reflexions require that the lattice must become primitive, but there seems to be no reason for reducing the point group symmetry below mmm. A choice must therefore be made between the 8 sub-groups of $Bmab$ having point group mmm. These are $Pman$ (no. 53), $Pccb$ (no. 54), $Pmcb$ (no. 55), $Pccn$ (no. 56), $Pmab$ (no. 57), $Pcan$ (no. 60), $Pcab$ (no. 61) and $Pmcn$ (no. 62). The distinction between these 8 possibilities depends on finding which mirror or glide planes are present in the true space group, and which are only pseudo-symmetry elements.

Long exposure precession and Weissenberg photographs of the $h0l$ reciprocal lattice layer showed four very weak reflexions, 104, 108, 302 and 502. These violate the requirements of the a-glide plane, and indicate that the true symmetry element normal to the y-axis is a c-glide.

Similarly, photographs of the $hk0$ layer showed 10 very weak reflexions, all having k odd, indicating that the b glide is a pseudo-symmetry element, and the true symmetry element normal to the z axis is an n glide.

On photographs of the $0kl$ layer no additional weak reflexions were observable. This, together with the larger U_{11} vibration parameters for some of the light atoms on the mirror plane, suggests that this mirror plane is a pseudo-symmetry element, and the true symmetry element normal to the x axis is a c glide.

If these conclusions are correct the true space group must be $Pccn$ (no. 56).

A further indication of the true space group comes from a consideration of the system of hydrogen bonds. The water molecules, $O(11+12)$, are linked in chains by hydrogen bonds of length 2·85 and 2·82 Å. In $Bmab$ one of these hydrogen bonds is across a twofold axis and the other is across a centre of symmetry. Since the hydrogen bonds are too long to be symmetrical, an ordered arrangement of the hydrogen atoms requires that both of these symmetry elements must disappear in the true space group. Of the eight subgroups considered above, only $Pccn$ and $Pcab$ involve the loss of both symmetry elements. As $Pccn$ has already been chosen on other grounds, this suggests that the hydro-

Table 1. *Parameters from the anisotropic refinement in space group Bmab*

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
K(1+2)	$\frac{1}{4}$	$\frac{1}{4}$	0·4844	0·065	0·037	0·011	0	0	0·044
K(3)	0	0·4146	0·3975	0·034	0·021	0·017	−0·002	0	0
P(4)	0	0·1749	0·1718	0·030	0·015	0·003	0·002	0	0
O(5)	0	0·1694	0·3207	0·065	0·031	0·003	−0·003	0	0
O(6)	0	0·2480	0·1461	0·042	0·016	0·020	0·009	0	0
C(7)	0	0·1049	0·3826	0·187	0·029	0·031	0·023	0	0
C(8)	0	0·1006	0·5113	0·332	0·049	0·008	0·011	0	0
O(9+10)	0·1274	0·1422	0·1227	0·036	0·033	0·013	−0·007	0·007	0·005
O(11+12)	0·1871	0·0145	0·1314	0·055	0·038	0·054	−0·014	0·013	0·007
O(13+14)	0·1655	0·3269	0·2851	0·031	0·041	0·016	−0·007	0·000	0·009

Table 2. *Final coordinates, vibration parameters, and their e.s.d.'s*

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$
K(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·4833 (6)	0·065 (6)	0·037 (3)	0·017 (4)	0·046 (7)
K(2)	$\frac{3}{4}$	$\frac{1}{4}$	0·4850 (6)	0·062 (6)	0·039 (3)	0·014 (4)	−0·045 (7)

	x	y	z	U_{iso}
K(3)	−0·0031 (7)	0·4145 (1)	0·3976 (3)	0·024 (1)
P(4)	0·0021 (7)	0·1749 (1)	0·1718 (4)	0·016 (1)
O(5)	0·0017 (17)	0·1694 (4)	0·3208 (11)	0·031 (2)
O(6)	−0·0017 (16)	0·2481 (4)	0·1463 (10)	0·024 (2)
C(7)	0·0236 (26)	0·1048 (8)	0·3826 (19)	0·040 (5)
C(8)	−0·0274 (33)	0·1006 (10)	0·5121 (23)	0·057 (7)
O(9)	0·1260 (16)	0·1450 (5)	0·1214 (11)	0·028 (3)
O(10)	−0·1254 (16)	0·1399 (5)	0·1254 (11)	0·023 (3)
O(11)	−0·1881 (16)	0·0124 (6)	0·1455 (13)	0·038 (4)
O(12)	0·1851 (16)	0·0163 (6)	0·1174 (12)	0·038 (3)
O(13)	0·1640 (15)	0·3273 (5)	0·2848 (13)	0·033 (3)
O(14)	−0·1682 (15)	0·3273 (5)	0·2879 (13)	0·034 (3)

gens are ordered. Indeed the inherent dissymmetry of the hydrogen bonds may be the ultimate cause of the observed lowering of the space-group symmetry.

The structure in space group $Pccn$

The weak $h+l$ odd reflexions were recorded on long exposure Weissenberg photographs of layers $1kl$ to $3kl$. A total of only 54 of the weak class of reflexion could be measured, and these were placed on the same scale as the $h+l$ even reflexions, by means of those strong reflexions common to both sets of photographs.

For a reflexion of the strong class, the value of $|F_c|$ depends on the magnitudes of the displacements from the pseudo-symmetric structure, but is independent of the signs of these displacements. A least-squares refinement in the true space group, but using the strong class of reflexions only, could lead to 2^{n-1} equal minima of the least-squares function, where n is the number of atoms which are displaced from their pseudo-symmetric positions. Inclusion of the weak class of reflexion, for which the values of $|F_c|$ depend also on the signs of the displacements, should enable the true

Table 3. *Observed and calculated structure factors*

minimum to be found. Clearly, if the displacements are small and there are but few weak reflexions measurable only limited success could be expected from such a refinement procedure. Alternatively, the weak reflexions alone could be used in a refinement in which the displacement parameters only were allowed to vary, but this method would be subject to the same limitations as the method described above, and would also require that the scale factor should be held fixed.

Both methods were examined in an attempt to obtain satisfactory $|F_c|$ values for the weak reflexions.

Firstly, the $h+l$ odd reflexions were used alone in a full-matrix refinement of the 16 displacement parameters. For the atoms lying on the false mirror plane at $x=0$, only the x coordinate was allowed to vary. For the atoms lying in pairs about the false mirror plane, one of each pair was fixed and the other allowed to refine, with interchange of the fixed and refined atom of each pair in alternate cycles.

After six cycles during which several of the parameters changed sign the R factor was reduced from 100% (zero displacements) to 44%.

The contributions to the weak reflexions of individual displacement parameters were calculated, and from these values certain sign changes of the parameters were indicated. After several such sign changes, each followed by least-squares refinement, the R factor for the weak reflexions was reduced to $14\cdot7\%$.

An electron density synthesis was then computed using the $h+l$ odd reflexions only. Such a synthesis has the symmetry of the true space group and the pseudo-symmetry elements appear as anti-symmetry elements. Around each atomic position appeared 'dumb-bells' of positive and negative density, the signs of the electron-density correctly corresponding with the displacements obtained.

Block-diagonal refinement was then continued using all of the data. All atoms were given isotropic temperature factors except K(1) and K(2). For these two atoms (in special positions) the anisotropy cannot be simulated by the displacements, and it was possible to refine the anisotropic vibration parameters. The refinement converged with $R=11\cdot9\%$ for all reflexions, whilst the R value for the weak reflexions alone rose to $15\cdot6\%$. It seems clear that the displacements of the atoms from their pseudo-symmetric positions are partly genuine displacements of the atoms from their pseudo-symmetric positions and partly a simulation of the anisotropy of their vibrations.

The final coordinates and vibration parameters, with their estimated standard deviations (e.s.d.'s), are given in Table 2. Of the 16 displacement parameters only three exceed $0\cdot1$ Å. These are the x coordinates of C(7) [$0\cdot24$ Å] and C(8) [$0\cdot27$ Å], and the difference in z coordinates of O(11) and O(12) [$0\cdot29$ Å]. The fixing of the relative signs of these displacements was the most important step in the refinement with the weak reflexions. It was expected that C(7) and C(8) would have opposite signs, since the *Bmab* coordinates of Table 1

Table 4. *Bond lengths and angles around the potassium ions*

K(1)—O(6)	3·05 Å (2×)		K(2)-O(6)	3·00 Å (2×)
K(1)—O(9)	2·89 (2×)		K(2)-O(10)	2·98 (2×)
K(1)—O(13)	2·76 (2×)		K(2)-O(14)	2·74 (2×)
K(1)—O(5)	3·44 (2×)		K(2)-O(5)	3·48 (2×)

O(6)—K(1)-O(6')	112°		O(6)—K(2)-O(6')	112°
O(6)—K(1)-O(9)	50 (2×)		O(6)—K(2)-O(10)	51 (2×)
O(6)—K(1)-O(9')	95 (2×)		O(6)—K(2)-O(10')	95 (2×)
O(6)—K(1)-O(13)	134 (2×)		O(6)—K(2)-O(14)	133 (2×)
O(6)—K(1)-O(13')	99 (2×)		O(6)—K(2)-O(14')	100 (2×)
O(9)—K(1)-O(9')	120		O(10)-K(2)-O(10')	121
O(9)—K(1)-O(13)	161 (2×)		O(10)-K(2)-O(14)	160 (2×)
O(9)—K(1)-O(13')	79 (2×)		O(10)-K(2)-O(14')	79 (2×)
O(13)-K(1)-O(13') ·	82		O(14)-K(2)-O(14')	82

K(3)—O(9)	2·95 Å		K(3)-O(10)	2·91 Å
K(3)—O(11)	2·82		K(3)-O(12)	2·79
K(3)—O(13)	2·73		K(3)-O(14)	2·70
K(3)—O(11')	3·53		K(3)-O(12')	3·30

O(9)—K(3)-O(10)	51			
O(9)—K(3)-O(11)	97			
O(9)—K(3)-O(13)	78		O(10)-K(3)-O(12)	93
O(9)—K(3)-O(12)	130		O(10)-K(3)-O(14)	80
O(9)—K(3)-O(14)	109		O(10)-K(3)-O(11)	134
O(11)-K(3)-O(12)	84		O(10)-K(3)-O(13)	111
O(11)-K(3)-O(13)	89			
O(11)-K(3)-O(14)	146		O(12)-K(3)-O(14)	95
O(13)-K(3)-O(14)	76.		O(12)-K(3)-O(13)	151

give an unreasonably short C(7)–C(8) length of 1·33 Å. Because of the pseudo-symmetry the e.s.d.'s of the displacement parameters given by the normal matrix may be unreliable, and a few of the signs of those displacements which are less than 2σ may be incorrect. The overall magnitudes of the displacement parameters depend directly on the scaling of the weak reflexions relative to the strong, and some additional uncertainty arises from this source.

Table 3 lists the observed and calculated structure factors, with the duplicate observations of those $F(hkl)$ which were observed on more than one layer. The 54 weak reflexions are grouped together at the end of the Table.

Description of the structure

A [100] projection of the structure is shown in Fig. 1, with the numbering of the reference atoms indicated. The potassium ions are in layers at $x=0$, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$, with four ions per cell in each layer. The ethyl phosphate ions are in layers at $x=0$ and $\frac{1}{2}$, with four ions per cell in each layer. The four water molecules are independent in the true structure, but are symmetry related in pairs in the pseudo-symmetric structure.

The potassium coordination

The bond lengths and angles around the potassium ions are given in Table 4. The e.s.d.'s of the K–O bond lengths are about 0·02 Å. Each potassium ion is coordinated to six oxygen atoms at distances of 2·7 to 3·0 Å, with two other contacts of about 3·4 Å. K(1) and K(2) occupy a single special position on a twofold axis in the higher symmetry space group, and two sets of special positions in the lower symmetry structure. K(3)

is in a general position, close to the false mirror plane, and in a special position of the higher symmetry space group.

The ethyl phosphate anion

The dimensions of the ethyl phosphate group are given in Table 5. The e.s.d.'s, increased somewhat to allow for the additional uncertainty in the displacement parameters, are 0·02 Å for the P–O lengths, 0·03 Å for O–C and 0·04 Å for C–C. The mean P–O terminal length is 1.52 Å, and the P–O(C) length is 1·56 Å. The accuracy of these lengths is insufficient for our original purpose. Each of the terminal oxygens [O(6), O(9) and O(10)] of the phosphate group makes five chemically significant contacts. In addition to the bond to phosphorus, each forms two hydrogen bonds to water molecules (2·71 to 2·78 Å) and also contacts two potassium ions (2·89 to 3·05 Å). The P–O–C oxygen atom, O(5), makes only two additional contacts, of length 3·44 and 3·48 Å, to potassium ions. The main effect of the displacements of C(7) and C(8) from the pseudo-mirror plane is to give a twist about the O(5)–C(7) bond, increasing the torsion angle about this bond from 0 to about 25°. This would have the effect of reducing repulsions between O(9) and O(10) and the hydrogens

Table 5. *Dimensions of the ethyl phosphate ion*

P(4)–O(5)	1·564 Å	O(5)–P(4)–O(6)	104·2°
P(4)–O(6)	1·536	O(5)–P(4)–O(9)	109·3
P(4)–O(9)	1·478	O(5)–P(4)–O(10)	105·9
P(4)–O(10)	1·552	O(6)–P(4)–O(9)	111·8
O(5)–C(7)	1·502	O(6)–P(4)–O(10)	112·4
C(7)–C(8)	1·470	O(9)–P(4)–O(10)	112·7
		P(4)–O(5)–C(7)	119·6
		O(5)–C(7)–C(8)	112·9
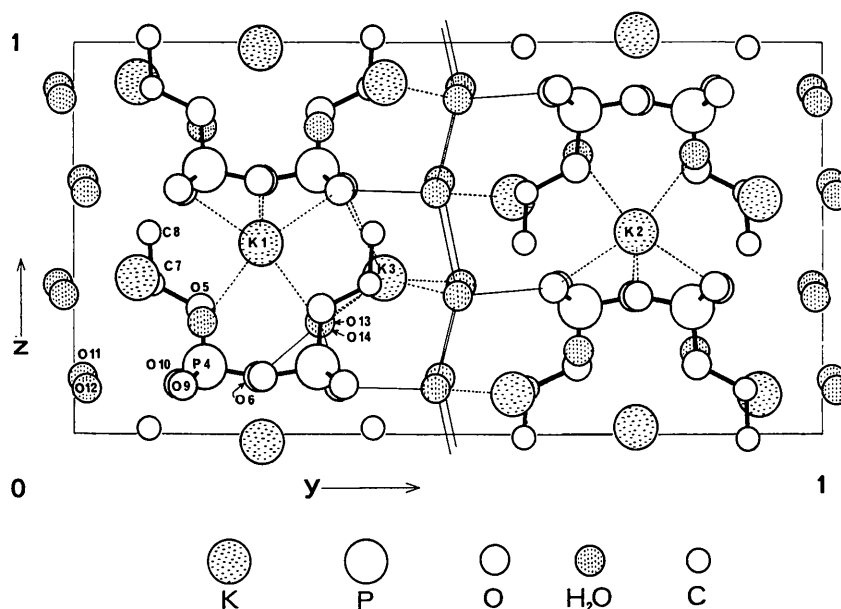
Fig. 1. Projection of crystal structure of $K_2(C_2H_5)PO_4.4H_2O$ down [100].

Table 6. *The water molecule coordination*

O(11)–K(3)	2·82 Å	O(12)–K(3)	2·79 Å
O(11)–O(10)	2·71	O(12)–O(9)	2·73
O(11)–O(12)	2·82	O(12)–O(11')	2·85
K(3)––O(11)–O(10)	122°	K(3)––O(12)–O(9)	126°
K(3)––O(11)–O(12)	72	K(3)––O(12)–O(11)	78
K(3)––O(11)–O(12')	107	K(3)––O(12)–O(11')	101
O(10)–O(11)–O(12)	97	O(9)––O(12)–O(11)	103
O(10)–O(11)–O(12')	112	O(9)––O(12)–O(11')	107
O(12)–O(11)–O(12')	144	O(11)–O(12)–O(11')	143
O(13)–K(3)	2·73 Å	O(14)–K(3)	2·70 Å
O(13)–K(1)	2·76	O(14)–K(2)	2·74
O(13)–O(6)	2·75	O(14)–O(6)	2·77
O(13)–O(9)	2·78	O(14)–O(10)	2·76
K(3)––O(13)–K(1)	104°	K(3)––O(14)–K(2)	105°
K(3)––O(13)–O(6)	104	K(3)––O(14)–O(6)	105
K(3)––O(13)–O(9)	127	K(3)––O(14)–O(10)	124
K(1)––O(13)–O(6)	104	K(2)––O(14)–O(6)	104
K(1)––O(13)–O(9)	110	K(2)––O(14)–O(10)	113
O(6)––O(13)–O(9)	105	O(6)––O(14)–O(10)	105

attached to C(7). However, for the $C_2H_5OSO_3^-$ ion in potassium ethyl sulphate (Truter, 1958) the corresponding torsion angle is only 6°.

The water molecules

The bond lengths and angles at the water molecules are given in Table 6, and hydrogen bonds are indicated by thin lines in the Figure. The water molecules O(11) and O(12) alternate in hydrogen bonded chains running parallel to the z axis. In the *Bmab* structure these hydrogen bonds have symmetries $\bar{1}$ and 2, but in the true structure both symmetry elements are lost. The other hydrogen of each of these water molecules

forms a hydrogen bond to one of the terminal phosphate oxygens. A further bond to a potassium ion completes the tetrahedral coordination of each water oxygen. The water molecules O(13) and O(14) also show tetrahedral coordination. They each form two hydrogen bonds to terminal oxygens of ethyl phosphate groups, and two bonds to potassium ions.

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