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Structure of the 2:1 Adduct of Potassium Hydrogenphosphite and Phosphorous Acid

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Abstract. $2KH_2PO_3.H_3PO_3$, triclinic, $P\bar{1}$, a = 8·590 (1), b = 9·010 (1), c = 7·576 (1) Å, α = 112·58 (1), β = 87·88 (1), γ = 101·21 (1)° at 297 K, Z = 2, $D_{\rm pyc.}$ = 2·000 (7) at 296 K, D_c = 2·016 Mg m^{-3}; R = 0·0240, R_w = 0·0237 for 2330 observed reflexions. The potassium ions form columns, and the hydrogenphosphite anions and phosphorous acid molecules form a hydrogen-bonded three-dimensional network.

Introduction. The study of the title compound was undertaken as part of an investigation of H_3PO_3–MH_2PO_3–H_2O systems. The potassium compound was selected because it was assumed to contain a polyorthophosphite anion connected *via* a hydrogen bond to the phosphorous acid. The sample was prepared by reaction of phosphorous acid with potassium hydrogenphosphite under conditions following from the solubility diagram of the H_3PO_3–KH_2PO_3–H_2O system at 298 K (Ebert & Muck, 1963). The cell dimensions were determined by least squares from the 2θ angles of 40 reflexions measured on an automatic Stoe four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. A total of 4364 intensities were collected with the same instrument from a prism-shaped crystal of volume 0·05 mm³ for 2θ = 3–55° and they were corrected for absorption (μ = 1·298 mm^{-1}).

Table 1. *Atomic coordinates* (×10⁴, *for* H ×10³) *with e.s.d.'s in parentheses, and isotropic temperature factors*

For non-hydrogen atoms $B_{\rm eq} = 4[V^2 \det(\beta_{ij})]^{1/3}$.

	x	y	z	$B_{\rm eq}/B$ (Å²)
K(1)	4033 (1)	0974 (1)	3152 (1)	2·13 (1)
K(2)	9238 (1)	1499 (1)	4084 (1)	2·33 (1)
P(1)	−1057 (1)	2224 (1)	−0621 (1)	1·81 (1)
O(11)	−0949 (2)	0942 (2)	−2545 (2)	2·22 (3)
O(12)	0102 (1)	2412 (2)	0955 (2)	2·52 (4)
O(13)	−2792 (2)	1886 (2)	0063 (2)	2·20 (4)
H(1)	−094	368	−066	2·37
H(13)	−282	257	132	3·16
P(2)	2813 (1)	5183 (1)	4661 (1)	1·78 (1)
O(21)	3231 (2)	6775 (2)	6334 (2)	2·35 (4)
O(22)	2431 (2)	3634 (2)	5031 (2)	2·39 (5)
O(23)	1408 (2)	5331 (2)	3515 (2)	2·79 (5)
H(2)	390	499	341	2·37
H(23)	090	438	261	3·16
P(3)	3659 (1)	2434 (1)	8563 (1)	2·05 (1)
O(31)	3783 (2)	1017 (2)	6795 (2)	2·86 (5)
O(32)	2910 (2)	1973 (2)	10214 (2)	2·87 (7)
O(33)	2702 (2)	3652 (2)	8353 (2)	2·73 (7)
H(3)	495	323	921	2·37
H(32)	194	218	1058	3·95
H(33)	269	361	703	3·95

The positions of the non-H atoms were obtained by direct methods and refined by least squares to $R = \sum ||F_o| - |F_c||/\sum |F_o|$ = 0·082 with isotropic temperature factors. In further cycles anisotropic temperature factors were refined to R = 0·033. The positions of all H atoms were obtained from a difference map. They were assigned the isotropic temperature factors of the atoms to which they are bound. The final R factor attained a value of 0·0240 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0·0237, with the weights w based on counting statistics.* In the final cycles, 103 independent reflexions (of 2433) which did not meet the condition $F > 2\sigma(F)$ were suppressed. A final difference map showed no residual electron density greater than 0·3 e Å^{-3}. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the program *SHELX* 76 (Sheldrick, 1976), modified for use on a small computer (Data General Nova 3).

Discussion. Final atomic parameters are given in Table 1. The more important interatomic distances,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36077 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

K(1)–K(2$^{\mathrm{i}}$)	4·238 (1)	K(1)–K(2)	4·457 (1)
–K(2$^{\mathrm{ii}}$)	4·240 (1)	–K(1$^{\mathrm{iii}}$)	4·771 (1)
–K(1$^{\mathrm{i}}$)	4·351 (1)	K(2)–K(2$^{\mathrm{iv}}$)	3·915 (1)
K(1)–O(21$^{\mathrm{vii}}$)	2·720 (2)	K(2)–O(11$^{\mathrm{ix}}$)	2·742 (2)
–O(31)	2·746 (2)	–O(11$^{\mathrm{viii}}$)	2·779 (2)
–O(11$^{\mathrm{x}}$)	2·813 (2)	–O(12$^{\mathrm{xi}}$)	2·824 (2)
–O(13$^{\mathrm{x}}$)	2·831 (2)	–O(23$^{\mathrm{vii}}$)	2·885 (2)
–O(31$^{\mathrm{i}}$)	2·848 (2)	–O(21$^{\mathrm{vii}}$)	2·954 (2)
–O(22)	2·860 (2)	–O(22$^{\mathrm{xi}}$)	2·962 (2)
–O(32$^{\mathrm{vi}}$)	2·955 (2)	–O(31$^{\mathrm{i}}$)	3·000 (2)
P(1)–O(11)	1·485 (2)	O(11)–P(1)–O(12)	117·7 (1)
–O(12)	1·521 (2)	–O(13)	108·2 (1)
–O(13)	1·572 (2)	–H(1)	112·6
–H(1)	1·308	O(12)–P(1)–O(13)	108·3 (1)
O(13)–H(13)	0·917	–H(1)	102·4
H(13)–O(21$^{\mathrm{v}}$)	1·691	O(13)–P(1)–H(1)	106·6
O(13)–O(21$^{\mathrm{v}}$)	2·573 (2)	P(1)–O(13)–H(13)	108·4
		O(13)–H(13)–O(21$^{\mathrm{v}}$)	160·2
P(2)–O(21)	1·494 (1)	O(21)–P(2)–O(22)	118·3 (1)
–O(22)	1·499 (2)	–O(23)	106·6 (1)
–O(23)	1·568 (2)	–H(2)	112·0
–H(2)	1·293	O(22)–P(2)–O(23)	110·8 (1)
O(23)–H(23)	0·906	–H(2)	106·6
H(23)–O(12)	1·752	O(23)–P(2)–H(2)	101·1
O(23)–O(12)	2·652 (2)	P(2)–O(23)–H(23)	115·5
		O(23)–H(23)–O(12)	172·1
P(3)–O(31)	1·471 (1)	O(31)–P(3)–O(32)	114·1 (1)
–O(32)	1·545 (2)	–O(33)	115·3 (1)
–O(33)	1·549 (2)	–H(3)	111·2
–H(3)	1·203	O(32)–P(3)–O(33)	105·6 (1)
O(32)–H(32)	0·900	–H(3)	103·8
O(33)–H(33)	0·989	O(33)–P(3)–H(3)	105·9
H(32)–O(12$^{\mathrm{xii}}$)	1·633	P(3)–O(32)–H(32)	118·9
O(32)–O(12$^{\mathrm{xii}}$)	2·528 (2)	–O(33)–H(33)	112·0
H(33)–O(22)	1·548	O(32)–H(32)–O(12$^{\mathrm{xii}}$)	172·5
O(33)–O(22)	2·530 (2)	O(33)–H(33)–O(22)	171·4

Symmetry code

(i)	$1-x$,	$\bar{y}$,	$1-z$	(vii)	$1-x$,	$1-y$,	$1-z$
(ii)	$x-1$,	y,	z	(viii)	$1+x$,	y,	$1+z$
(iii)	$1-x$,	$\bar{y}$,	$\bar{z}$	(ix)	$1-x$,	$\bar{y}$,	$\bar{z}$
(iv)	$2-x$,	$\bar{y}$,	$1-z$	(x)	$\bar{x}$,	$\bar{y}$,	$\bar{z}$
(v)	$\bar{x}$,	$1-y$,	$1-z$	(xi)	$1+x$,	y,	z
(vi)	x,	y,	$z-1$	(xii)	x,	y,	$1+z$

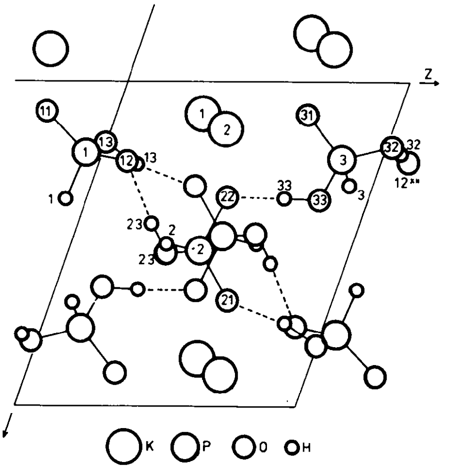

Fig. 1. Schematic projection of the structure in the *YZ* plane.

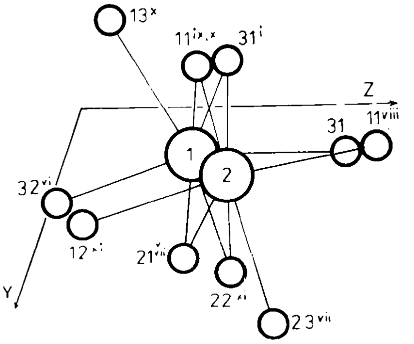

Fig. 2. The coordination of O atoms around the potassium ions.

bond angles and the symmetry code are given in Table 2. A schematic projection of the structure in the *YZ* plane is depicted in Fig. 1.

The K^+ ions form columns parallel to the *a* axis. Each K^+ ion has seven O neighbours with an average K · · · O distance of 2·82 (7) Å for K(1) and 2·88 (9) Å for K(2) (Fig. 2). The other O atoms are more distant than 3·703 Å.

Average distances are P–O = 1·49 (2), P–O(H) = 1·56 (1), P–H = 1·27 (5) and O–H = 0·93 (4) Å. The phosphite anions and the phosphorous acid molecules are connected by relatively strong hydrogen bonds with an average O · · · O distance of 2·57 (5) Å, so that they form a three-dimensional network. All values of the interatomic distances and angles are in accordance with literature data.

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