# The Crystal Structure of KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>

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 $m KH_5(PO_4)_2$  crystallizes in space group  $P2_1/c$  with a=7.849, b=10.688, c=9.557 Å,  $\beta=114.35^\circ$  and Z=4. The structure has been determined by means of three-dimensional Patterson and electron density summations. A final R value of 0.075 was obtained using 1246 independent reflections.

The structure is built up from phosphate tetrahedra connected by strong hydrogen bonds, the average  $\hat{\mathbf{O}} - \mathbf{O}$  distance being 2.562 Å, though one distance is as short as 2.405 Å. Approximate positions of the hydrogen atoms could be deduced from a difference electron

density summation.

It was possible to distinguish different kinds of bonds within the  $PO_4$  groups, viz., P-OH bonds with lengths of 1.549, 1.550, 1.559, and 1.560 Å, and P-O bonds of 1.490 and 1.502 Å. The two oxygen atoms which are involved in the short hydrogen bond have P-O distances of 1.512 and 1.515 Å.

 $\mathbf{R}^{\text{ecently}}$ , the chemistry of semi-metallic orthophosphates of the type  $\mathbf{M}^{\text{T}}\mathbf{H}_{5}(\mathrm{PO}_{4})_{2}$ , where  $\mathbf{M}^{\text{T}}=\mathrm{NH}_{4}$ , Na, K, Rb, and Cs, has been studied. Methods of preparation, stability conditions and reactivity have been reported <sup>1</sup> and cell dimensions have been determined,<sup>2,3</sup> but, hitherto, no crystal structure investigation has been performed.

Since there is only one metal(I) ion per two phosphate groups in the structure, the question arises whether there is one  $\rm H_3PO_4$  molecule and one  $\rm H_2PO_4^-$  ion, or whether the two phosphate groups are equivalent. Previous investigations of phosphoric acid <sup>4,5</sup> and compounds containing  $\rm H_2PO_4^-$  ions, like  $\rm Ca(H_2PO_4)_2 \cdot H_2O,^6$   $\rm N_2H_5H_2PO_4,^7$  and  $\rm N_2H_6(H_2PO_4)_2,^8$  have shown that it is possible to distinguish between  $\rm P-OH$  and  $\rm P-O$  bonds on the basis of the bond lengths. From this point of view it seemed interesting to study the crystal structure of a semi-metallic orthophosphate.

For the investigation, crystals of suitable size for an X-ray single crystal analysis were prepared of the potassium salt,  $KH_5(PO_4)_2$ . Crystals of this

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compound have been grown with dimensions as large as  $5 \times 5 \times 5$  cm<sup>3</sup>, and a Raman spectroscopic study has been started 9 which provides additional reasons for the choice of potassium as cation.

#### EXPERIMENTAL

The method of preparation of KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> has been described earlier.¹ The unit cell dimensions, the space group and the observed and calculated densities have also been

reported in a previous paper.<sup>2</sup>

Crystals of KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> are not completely stable when mounted in air and irradiated for a long period of time. If, however, they are mounted in a glass capillary, the crystals appear to be unaffected, which may indicate that they are slightly hygroscopic. The crystal selected for the investigation did not have completely well-defined faces, but could, as a good approximation, be described as indicated in Table 1.

Table 1. Dimensions of the crystal used for the intensity measurements, given as indices of the boundary planes and the distances to these planes from an internal origin.

h	$\boldsymbol{k}$	l	d (mm)
1	0	0	0.080
<b>–</b> 1	0	0	0.080
0	1	0	0.150
0 .	<b>–</b> 1	0	0.150
0	0	1	0.045
0	0 -	- 1	0.045

Weissenberg equi-inclination films corresponding to the h0l-h9l reflections were registered with  $CuK\alpha$  radiation. A summary of the crystallographic data is given in Table 2.

Table 2. Crystallographic data for KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>.

Unit cell <sup>2</sup>	Monoclinic with
	a = 7.849(2) Å
	b = 10.688(2)  Å
	c = 9.557(2) Å
	$\beta = 114.35(2)^{\circ}$
	$V = 730.30 \text{ Å}^3$
Formula weight	M = 936.16
Density (20°C) <sup>2</sup>	$D_m = 2.128(2) \text{ g.cm}^{-3}$
	$D_x = 2.128 \text{ g.cm}^{-3}$
Systematic absences	$h\hat{0}l$ when $l=2n+1$
	0k0  when  k = 2n + 1
Space group	$P2_1/c$
General point positions	$\pm (x,y,z); \pm (-x,\frac{1}{2}+y,\frac{1}{2}-z)$
Crystal habit	White plates
Linear absorption coefficient	$\mu = 105.8 \text{ cm}^{-1} (\text{Cu}K\alpha, \lambda = 1.5418 \text{ Å})$

The intensities were estimated visually by comparison with an intensity scale prepared from timed exposures of a suitable reflection from the crystal. The values from the six films, recorded for each layer line, were scaled together using the program SCALE, with weights according to the formula  $w = [1.0 + [(I - 12.0)/6.0]]^{-1}$ . The inter-layer scale factors were initially chosen in agreement with the corresponding exposure times.

A total of 1395 independent reflections were registered, 149 of which were too weak to be measured.

#### STRUCTURE ANALYSIS AND REFINEMENT

All independent reflections, corrected for Lorentz and polarization effects, were used to calculate a three-dimensional Patterson synthesis. The positions of the potassium and phosphorus atoms were deduced from the Patterson peaks, the atoms occupying three general positions (K,  $P_1$ , and  $P_2$ ) in space group  $P2_1/c$ . The oxygen atoms were then located from subsequent electron density calculations. A preliminary isotropic refinement of the structure, including the refinement of separate scale factors between the layer lines, gave an R value of 0.133  $(R = \sum ||F_0| - |F_c||/\sum |F_o|)$ .

The reflections were then corrected for absorption and extinction, using the formula given by Zachariasen,  $^{10}$  applied as described by Asbrink and Werner,  $^{11}$  with c=0.008. The isotropic refinement was then repeated, and, especially for the strong reflections, improved agreement between the calculated and observed structure factors was obtained (R=0.108). Eight of the strongest reflections, however, still suffered from errors which had not been accounted for, and were therefore excluded from all further refinements.

In the final refinement, in which allowance was made for anisotropic temperature vibrations, the R value converged to 0.075 (0.092 including the eight strong reflections omitted and all unobserved reflections). The resulting positional and thermal parameters are given in Table 3, and the corresponding

Table 3. Final atomic parameters for KH<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>. The anisotropic temperature factor is:  $\exp[-2\pi^2(h^2a^{*2}\ U_{11}+k^3b^{*2}\ U_{22}+l^2c^{*2}\ U_{33}+hka^*b^*\ U_{12}+hla^*c^*\ U_{13}+klb^*c^*\ U_{23})].$  Standard deviations of the least significant figure in parentheses.

Atom	x/a		y/b	z/c		$B$ $^2$
K	0.7906	(2)	0.3769 (1)	0.3607	(1)	2.85 (5)
$\mathbf{P_1}$	0.3529	(2)	0.2256 (1)			2.04 (5)
$\mathbf{P_2}$	0.8895	(2)	0.0703(1)			<b>2.21</b> (5)
$O_1$	0.1463	(5)	0.2162(4)			2.96 (ll)
O,	0.4584		0.2883 (4)			2.63 (10)
O <sub>3</sub>	0.4242	(5)	0.0880 (4)	0.2478	(5)	<b>2.9</b> 0 (11)
O <sub>4</sub>	0.4035	(6)	0.2994 (4)	0.3575	( <b>4</b> )	2.66 (10)
$O_5$	0.7749	(7) -	-0.0032(4)	0.1207	(5)	3.63 (13)
O <sub>6</sub>	0.0808	(6)	0.0028(4)	0.3455	(5)	3.42 (12)
O,	0.9180	(5)	0.1985 (4)	0.2166	(4)	<b>2.9</b> 1 (11)
$O_8$	0.7924		0.0769 (4)	0.3762	(4)	2.46 (10)
-	$U_{11}$	$U_{22}$	$oldsymbol{U_{33}}$	${U}_{12}$	$U_{13}$	$U_{23}$
K	0.041 (1)	0.033 (1)	0.032 (1)	-0.002(1)	0.023 (1)	0.006 (1)
$\mathbf{P_1}$	0.027 (1)	0.032(1)	0.023 (1)	0.003 (1)	0.023(1)	-0.004(1)
$\mathbf{P}_{\mathbf{z}}^{T}$	0.031(1)	0.026 (1)	0.027 (1)	-0.001 (1)	0.026(1)	0.000(1)
O <sub>1</sub>	0.030 (2)	0.062(4)	0.029 (2)	0.003(4)	0.023(3)	0.002(4)
Oa	0.038(2)	0.036(3)	0.028(2)	-0.012(3)	0.031(3)	-0.006 (3)
$O_3$	0.036(2)	0.023(3)	0.049(3)	0.001(3)	0.035(3)	-0.005(4)
O <sub>4</sub>	0.045(2)	0.033(3)	0.023(2)	0.010 (3)	0.027(3)	-0.001 (3)
O <sub>5</sub>	0.075(2)	0.040(3)	0.029(2)	0.034(4)	0.041(4)	0.005(4)
$O_6$	0.049(3)	0.055(3)	0.040 (2)	0.049 (4)	0.055(4)	0.031(4)
Ο,	0.034(2)	0.022(3)	0.057(3)	0.000(3)	0.042(4)	0.004(4)
$O_8$	0.028 (2)	0.042 (3)	0.031 (3)	0.006 (3)	0.027 (3)	0.006 (3)

Table 4. Observed and calculated structure factors for  $\mathrm{KH_5(PO_4)_2}$ . The columns are k,  $|F_\mathrm{o}|$ , and  $F_\mathrm{c}$ , respectively. \* indicates reflections not included in the refinement (unobserved reflections and eight of the strong reflections).

	CCL	-5 0 L	5 1 L	6 278 -291 7 81 87	4 183 -204 5 1C3 1C2	5 123 137 6 41 -39	231	4 286 -295 5 576 -632
	1360-1646*	C 194 175 2 40 C*	0 305 304	8 259 253	6 36 -21*	7 53 -58	C 358 325 1 123 13C	6 621 589 7 95 101
4	666 -650	4 334 -328	1 88 85 2 102 100	9 175 154 10 90 -91	7 78 ~75 8 68 60	8 120 -120 5 114 110	2 560 -466	7 95 101 E 85 +85
Ē	460 5C2	6 125 -138 8 453 515	3 116 -123	11 306 -291		10 216 194	3 243 243 4 E6 53	9 147 149
10	75 -69	10 266 -226	4 39 5* 5 34 23*	12 67 75	4 2 L 0 266 252	11 98 -91 12 77 -87	5 209 -215	10 185 -174 11 22 -28
	101	12 63 -58	6 173 -157	-6 1 L	0 266 252 1 335 334		6 33 -13* 7 38 -35	
0	290 297	-6 0 L		0 65 -72	2 35 -144	~5 2 L	£ 12C 116	-4 3 t
4	743 -845 280 265	C 181 -172	6 1 L 0 71 72	1 226 235 2 353 -366	3 39 -14* 4 188 -191	0 68 -67 1 202 232	9, 110 116	0 164 165 1 414 399
6	65 -60	2 292 286 4 169 -147	1 170 -169	2 256 -245	5 57 43	2 147 163	3 3 Ł	2 270 260
1C	266 227 267 -267	6 49 -46	2 42 12+ 2 55 57	4 536 551	6 71 71 7 121 -121	3 131 151 4 215 -236	C 31 16	3 125 -133 4 426 -439
••		8 53 -36 10 211 188	4 174 -16C	5 128 140 6 120 -124	1 121 -121	5 172 -182	1 437 -367 2 529 -486	5 132 -138
	2 0 L	10 211 188	5 31 30	7 78 -65	5 2 L	6 220 229	3 252 -247	6 265 -286 7 127 -121
2	334 -370 461 -419	-7 0 L	711	8 51 -85 9 125 112	0 68 -67 1 421 421 2 35 44	7 38 13* 8 218 -211	4 114 111 5 162 162	7 127 -121 8 606 561
4	316 28C 231 15C	0 329 -317 2 355 361	C 1C2 - 57	11 106 -97	2 35 44	9 38 40	5 162 182 6 176 186	9 260 253
6	231 15C 200 -170	2 355 361 4 126 12C 6 367 -404	1 173 -166 2 36 7*		3 156 -156	10 154 142 11 42 45	7 114 108	10 225 -231 11 59 -55
•		6 367 -404 8 153 136	3 152 140	-7 1 L 0 1C2 57	4 36 28* 5 31 -41	11 42 45	8 112 -109	
c	3 0 L 664 -668	8 153 136	4 146 -145	1 114 127	£ 117 -116	-6 2 L	4 3 L	-5 3 L 0 261 291
2	218 201	-E C L	8 1 L	2 196 -196 3 El -65	6 2 L	0 246 -262 1 36 22*	0 202 -185	0 261 291 1 126 139
4	218 2C1 357 375	2 348 -255 4 386 365	0 87 -75 1 37 -39	4 86 -82	0 295 -262	2 226 243	1 47 -41 2 183 -198	2 217 -215
6	257 -246 34 22*	6 176 -145	1 37 -39	5 77 84 6 302 294	1 156 144 2 107 110	3 60 -59 4 129 129	3 167 -225	3 28 -29 4 449 463
٠		£ 46 31* 10 167 -130		7 72 -70	3 158 -157	5 122 137 6 241 -265	4 521 555 5 154 164	5 158 168
0	4 0 L 510 -519	10 167 - 130	9 1 L 0 166 -179	8 155 -162	4 155 -157		6 390 -383	6 465 -511 7 201 -207
2	769 890	-9 0 L		9 40 -12* 10 106 87	5 74 77	7 117 -109 8 164 155	7 65 -59	8 147 152
4	371 -376 152 -119	4 73 -62 6 E7 73	-1 1 L C 125 52	11 65 68	721	9 38 3+	5 3 L	9 34 2*
6 8	152 -115 155 150		1 223 -191	-e 1 L	0 76 69 1 37 -29	1C 143 -131 11 E1 77	0 269 -291	1C 62 65 11 108 1C6
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ž	154 175 250 265	3 139 -127 4 90 E6	5 413 -423	4 1C5 -116 5 57 67	4 104 106	1 116 -119	4 153 -155 5 27 29	1 110 -114
4	514 -497 316 299	5 252 -226	6 36 15* 7 270 279	6 39 32*	8 2 L	2 303 -322	6 51 -62	2 97 109 3 186 -185
۰		6 378 -394 7 221 228	E 22E -26C	7 54 -48 6 161 145	C 32 -26* 1 158 -136	3 37 29* 4 411 457	6 3 L	4 171 175 5 153 212
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0	198 - 172 57 52	9 66 -59		10 133 -134	0.21	6 168 -175 7 72 79	1 129 133	6 199 -209 7 116 116
		10 28 -22	-2 1 L C 1C22-128C*	-9 1 t	92L 0 41 45	8 38 -14+	2 65 6C 3 31 27*	8 36 -13+
	7 0 L	1 1 L	1 705 -788	6 61 -71		9 233 -213 10 41 -28	4 137 -144	9 16C -155 10 28 28
ž	366 -317 45 21*	0 125 -52	2 403 477	7 1C5 56 8 41 40	-1 2 L 0 961 813	10 41 -28 11 185 182	5 77 -73	11 98 -88
4	66 50	1 19 -9* 2 182 201	3 905 1134* 4 154 -185	9 156 -153	1 391 -375		736	
	8 O L	3 177 143	5 548 -5CE	C 2 L	2 784 -735 3 65 95	-82 L 2 63 6C	0 34 -34*	-73 L 1 45 51
c	44 23	4 273 -255	6 314 318 7 47 44	1 715 -467#	4 227 -170	3 58 -58	1 89 79 2 78 -74	2 264 -314
Ž	105 50	7 39 -24*	7 47 44 8 211 -220	2 101 100 3 943 823	5 147 139 6 135 130	4 36 -45 5 89 -90	3 56 -52	3 163 -183 4 334 381
	90 L	£ 37 -11* 6 191 199	9 29 -8*	4 28 15*	6 135 130 7 208 -221	6 36 -20+	8 3 L	5 166 174
С	237 222	9 95 -94	10 64 -52 11 53 53	5 658 -718	8 174 152	7 229 219	0 266 -250	6 142 -147 7 49 -48
	-1 C L	10 28 -32		6 34 -29* 7 154 166	9 126 120 10 80 -74	8 48 48 9 126 -118	1 69 -66	8 72 68
0	289 257 577 737	2 1 L	-31 L 0 583 583	£ 1C7 1C7			2 134 13C	\$ 31 8* 10 194 -177
4	386 -359	0 1022 1280*	1 118 -161	9 154 142 10 149 -144	-2 2 L 0 340 -269	-92L 3 73 69	-1 3 L 0 1298-1294	11 58 -63
6	44 -21*	1 24 27* 2 1118-1162	2 80 -119 3 335 303		1 462 -493	4 93 95	0 1298-1294 1 767 -714	
10	178 -146 256 213	3 193 -161	4 241 -219	1 2 L C 561 813	2 339 -269 3 463 371	5 101 -97 6 122 -122	2 ECE 663	-8 3 L 2 226 -217
		4 230 211 5 481 458	5 30 37	1 199 -152	4 80 51	7 35 3G	3 55 47 4 332 303	3 32 -38
0	-2 C L 371 -370	6 199 208	6 153 -167 7 155 -212	2 123 37	5 42 12	8 243 226 9 37 36	5 196 178	4 32 -6* 5 51 -49
2	66 74	7 245 -254 8 41 -36	8 316 239	3 166 -157 4 154 -153	6 608 574 7 142 -154	7 31 36	6 69 -59 7 98 102	6 130 126
4 6	779 890 533 -550	9 37 -34	9 57 53 10 207 -196	5 129 -137	8 535 -537	C 3 L	8 212 -215	7 66 56 8 59 -58
ě	49 -43		10 101 -170	6 70 69 7 306 340	9 36 -25* 10 201 195	1 513 -455 2 1662 1148*	9 101 -100 10 76 77	9 25 -70
10	116 92	3 1 L C 583 -583	-4 1 L 0 83 -66	E 34 −39	11 80 77	3 848 677	10 76 77 11 57 -56	1C 43 52
	-3 0 L	1 29 8*	1 28 -28*	9 138 -141 10 29 25	-3 2 L	4 576 -463 5 246 -223		-9 3 L
ç	596 -668	2 135 -136 3 127 -115	2 278 304	10 29 23	0 356 -358	6 62 56	-2 3 L 0 357 -325	4 249 -248
2	452 -536 699 919+	4 556 639	3 1CS S1 4 239 -238	221	0 356 -358 1 103 108	7 32 -29*	1 26 28	5 80 ~80 6 124 118
6	412 448	5 157 168	5 174 -163	C 348 -269 1 281 -243	2 335 365 3 444 -440	E 253 - 286 9 45 - 48	2 358 -335 3 537 -510	7 24 17*
3	677 -891 343 287	6 278 -280 7 154 -157	6 269 266 7 7C 64	2 27 -45*	4 375 -375	10 316 321	3 537 -510 4 96 91	8 48 -41
10 12	343 287 41 35	E 27 -18*	8 230 -235	3 70 -64 4 545 567	5 317 314 6 144 163	1 3 L	5 16C 154	0 4 L
		9 53 104	9 41 33+	5 83 80	7 38 -27	C E1C 1254*	6 424 439 7 230 259	1 539 -423
c	-4 0 L 475 -519	416	10 90 91 11 85 -82	6 442 -417	8 47 -44	1 231 213	8 342 -338	2 51 -54 3 22 -11*
ž	33 57	0 91 66	12 23 -31	7 130 140 E 14E 16C	9 37 17* 10 23 17*	2 166 -162 3 428 380	9 142 -142	4 40 14
4	543 -613 671 769	2 182 172	-5 1 L	9 156 -171	11 184 -174	4 356 -339	10 E2 74 11 36 -37	5 28 19* 6 37 -41
ε	178 -17C	3 267 -291	0 305 -304	3 2 L	-4 2 L	5 74 -67 6 60 -50	-3 3 L	7 181 208
10	165 -127 51 47	4 51 -57 5 1C8 116	1 254 27C 2 561 596	0 396 -358	0 266 292 1 556 615	7 156 -173	-3 3 L C 27 -16 1 594 592	8 121 -119 9 218 -214
**	21 T/	6 35 -13+	3 472 -494	1 254 -255 2 401 417	1 556 615 2 94 -89	8 145 154 9 44 48	1 594 592 2 400 -423	9 21E -214 10 17E 173
		7 44 -43 8 48 -51	4 141 -150 5 139 140	3 139 153	3 432 -432	10 56 55	2 400 -423 3 346 324	
			> 176		6 27 -254			

Table 4. Continued.

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1					244 265 EE 50	10 44 41 11 113 114	4 53 67	-7 <b>6</b> L	-2 7 L	
3   20   20   10   10   10   10   10   10		205 140	e 33 ~	134 6	165 155	-5 5 L	6 23 15+	1 210 216	C 155 184	
1		302 264				1 325 -380		4 102 -90	3 330 -338	
195   196   2   196   297   1   197   19		264 -215			3 5 L	3 126 135	0 35 13*	6 124 114	5 3EC 4C3	0 34 26
1	7	30 25+	1 24	224 1	121 120 50 -36	5 157 -220	2 68 -55	8 125 -122	7 257 -262	2 23 -16*
1	5	22 -3*	3 199 -2	13 3	176 -186	7 293 313	4 148 141		9 29 44	4 116 105
\$ 1.0 Section 1.0	10		5 230 2	45 5	139 144	9 112 -1CC		3 126 134	••	
1		432 323	7 111 -1	03 7	24 17*		0 56 -52	5 169 -155	C 245 -257	4 8 L
1	2	459 357	9 115	58		-6 5 L C 218 230	2 22 40	7 53 50	2 313 352	1 210 -205
6 A 24 A 27 A 24 A 24 A 24 A 27 A 27	4	557 -603 328 -332		39 C	161 168	1 73 -66 2 306 -302	4 10 65		4 178 -157	3 86 89
1		224 235	-5 4 L 0 235 -2	2	81 -75	3 78 -70	7 6 L 0 31 16*	l 148 144 2 147 -137	6 38 12* 7 37 19*	5 3C -3C
1			1 127 1 2 184 -2	54 4	29 -9#	6 159 -172	1 197 195 2 26 -27	3 73 -69 4 33 -9*	E 4E -5C 9 153 -13C	0 256 243
1 472 392		3.4 L	4 369 4	45 7		£ 177 17E		£ 153 155		2 124 -128
1. 25 - 165		472 392	6 190 -2	03	5.5 L	10 109 -116		8 107 -98	-4 7 L C 23E -246	
5 45 -67 10 26 114 4 -15 4 172 172 2 32 -18 2 364 -565 0 127 -135 4 216 217 2 176 -216 177 2 32 -18 4 17 2 32 -18		205 -195	8 24 -	10+ 1	321 338		0 152 12C		2 105 -103	6 8 L
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4 1 0 98 102	ì			5	32 -37	3 32 12+	4 236 216	2 247 -235	6 78 -74	
1   11   31   2   267 - 367   C   243 - 236   7   772   270   8   75   61   6   155 - 165   10   40   -43   2   185 - 141   3   3   1   5   1   5   6   8   8   1   1   1   1   1   1   1   1	c	333 -326	0 99 1	02		5 155 -172	6 55 44	4 279 412	E 64 -56	C 158 -155
3 185 -183	1 2	7E -7C	2 367 -3	157 (		E 3C 14#	9 27 -32	6 155 -145	10 40 -43	-1 8 L
6 25 -21  7  22 25 27  7  22 25 27  7  22 25 28 27  1  2 28 -25 28 3 31 4 323 28 26 26 27  27  1  2 28 -25 28 3 31 4 323 28 26 28 28 28 28 28 28 28 28 28 28 28 28 28	4	140 154	5 154 -1	49 3	26 17*			8 93 -E7 9 47 -54	C 73 76	0 65 -60 1 77 -82
0 241 -66			1 62	59		-8 5 L	0 30 27	2 7 L	2 138 -135	3 314 323
2 215 222			9 56 -	-56 0	147 -132		2 180 -161	1 6CE -717	4 35 -26*	5 168 -195
3 33 -15*	ì	75 - 86		42 2	161 156	5 95 -87	4 76 -59	3 503 601	6 145 152	
5 CC 66 2225 215 1 1 C 16 10C - 256 5.4 9 73 84 8 24 - 228 7 108 - 368 - 308 -	3	33 -15*	-7 4 L	_		7 27 -190	6 169 167	5 106 -103	8 1C2 -EE	
6 A L 5 305 -305 -15 L 5 122 122 - 27 L 122 - 122 122 - 27 L 122 -	5	SC 86	2 225 2	, IC C	56 54	9 73 84	8 24 -28* 9 155 151	7 108 -98		0 339 -348
1 155 262 7 225 212 1 97 -A0 7 134 -153 0 EE 75 1 347 -346 3 260 289 4 263 266 2 5 7 5 6 8 70 78 2 5 2			4 308 -3 5 345 -3	808	-1 5 1	-9 5 L 5 123 139		2 7 L	C 75 77 1 133 -125	2 52 38
1   148 - 137	1	195 208	7 229 2	12 1		6 20 17* 7 134 -153	0 88 75	1 347 -346	3 280 289	4 263 266
7 4	3	148 -137	9 109 -1	.07 3	198 -181	( 6 L	2 94 -72	3 371 366	5 261 -257	6 155 -161
7 4 L 2 65 63 7 118 -11C		136 135		5	231 236	2 458 449	4 154 151	5 136 -156	7 188 191	8 27 -5*
1 173 -158	0	7 4 L 31 -23	2 65	63 7	118 -108	4 271 -3EC	6 263 -293 7 226 -250			-3 & L
8 4	1 2	E3 75	4 3C 5 3C	2* 9	47 -43	6 219 227 7 78 79	8 221 215 9 196 192	4 7 L 0 238 246	-7 7 L 2 74 69	1 74 00
0 103 90	?		7 28 -	05 42*	-2 5 L	8 68 -65 9 24 -32		2 201 -200	5 126 111	3 64 -61
-9.4 L 3 182 164 1 466 -744 2 221 -245 6 6 6 7 9 31 29 7 13C 13C 13C 12C 13C 13C 12C 13C 13C 12C 13C 13C 12C 13C 13C 13C 13C 13C 13C 13C 13C 13C 13	ç	103 90		- 55 1	94 83	161	0 270 262	4 33 -39	7 201 -193	5 71 -66
1 245 167 6 23 -24 6 18E 2CC 4 2C5 -2C6 5 340 392 0 90 -768.7 L 2 727 -555% 7 198 201 7 121 -121 5 112 102 6 373 -4C7 1 51 -27 4 36 38 -48 1 3 280 27C	٠		-9 4 L	3	182 164	1 686 -744	2 221 -245	6 66 67	9 31 29	7 130 130
2 727 -555% 7 198 201 7 121 -121 5 112 106 6 373 -407 1 1 1 -12 4 36 38  -4 8 1 3 200 271		120 -130	5 112 -1	116 5	96 82	3 340 318 4 205 -206	4 351 402	5 / L 0 90 -76		
4 100 88	2	727 -555*	7 198 2	01 7	121 -131	5 112 1CE	6 373 -407	1 51 -67	4 36 38 5 98 101	-4 8 L C 243 258
\$\begin{array}{c c c c c c c c c c c c c c c c c c c		212 -224		9	61 55	8 158 -158	9 70 -63	3 84 -75	6 25 -21*	1 249 -26C 2 271 -287
9 125 121	7	44 -55	1 153 1 2 312 -2	94			10 55 51 11 127 161		CEL	4 51 83
7 357 -356 3 104 -111 3 200 155 2 74 -72 3 147 -132 5 256 246 9 22 -44 26 7 3 4 140 136 4 116 -103 3 70 -55 6 1 21 214 2 257 250 5 46 25 5 35 -34 4 47 42 7 7 1 7 1 7 84 -84 -56 1 2 425 -471 1 5 1 7 34 31 7 186 -171 6 67 64 1 66 56 7 5 6 6 25 25 24 3 349 -329 C 346 -330 8 142 134 8 49 -42 7 7 177 177 2 56 66 2 2 182 -199 4 39 -22 1 112 10 5 30 266 8 142 134 8 49 -42 7 177 177 17 2 56 66 2 2 182 -199 4 39 -22 1 112 10 5 30 266 8 118 -115 7 177 177 177 17 2 56 66 1 1 8 1 3 106 -111 5 1 6 130 136 3 319 304 11 74 -71 C 67 75 16 16 17 16 17 17 17 17 17 17 17 17 17 17 17 17 17	9	125 121	4 96 1	IC2 0	121 -120	0 34 27		C 83 -77	2 188 183	6 33 35
-2 4 L 8 29 -529 4 140 136 4 116 -103 3 7 0 -55			6 94	93 2	161 16C	2 15C 165	1 48 -46	2 29 34	4 214 - 358	8 28 25*
1 65 -61	c	-2 4 L 344 323	8 29 -	52* 4	140 136	4 116 -103	3 70 -59		6 219 214	-5 A L
3 349 -329	1	65 -61		6	275 -299	6 33 33	5 94 92 6 E7 E4	C 25 -17*	£ 23 -6#	C 229 243 1 64 74
5 426 4C5 2 175 165 10 25 140 3 6 6 79 233 -251 -1 7 6 60 -60 4 66 63 6 130 136 3 319 304 11 74 -71 1 C 66 75 1 65 65 7 62 7 7 7 7 7 8 7 7 9 7 8 157 -155 1 146 1 1 151 152 2 76 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	4	349 -329 39 -22	C 346 -3	3C 8	142 134		7 177 17C 8 118 -115	2 56 66	1 8 L	2 182 -199 3 106 -111
8 169 187 5 285 -317 -45 L 2 64 54 -66 L 2 46 -38 3 31 9 7 151 -146 5 156 163 6 70 70 6 161 -168 3 91 81 0 50 -52 3 33 -23 4 191 -195 6 111 59 10 282 -284 7 92 -94 1 242 247 4 2(1 -194 1 118 111 4 153 -155 5 31 -11 9 121 134 118 113 4 153 -155 5 31 -11 9 121 134 118 111 4 153 -155 5 31 -11 9 121 134 118 111 4 153 -155 5 31 -11 9 121 134 118 111 4 153 -155 5 31 -11 9 121 134 118 111 4 153 -155 5 31 -11 9 9 121 134 118 111 4 153 -155 5 31 -11 9 121 134 118 111 4 153 -155 5 31 -11 9 9 121 134 118 118 118 118 118 118 118 118 118 11	6	130 136	3 319 3	04 11		3 6 L C EE 75	9 233 -251	C 127 135	C 60 -60 1 14C 125	4 68 63 5 97 83
10 282 -284 7 92 -94 1 242 247 4 2(1 -194 1 118 111 4 153 -155 5 31 -11e 9 121 134 111 163 -173 8 157 -155 2 25 -12e 5 282 -235 2 105 -112 5 25 -35 31 e 6 262 265 9 20 231 3 288 301 6 128 121 3 253 -277 6 88 80 7 160 -147 -6 8 L C 365 355 2 5 L 5 362 -367 7 92 66 4 170 162 7 203 -198 8 76 -73 2 31 16e 2 255 1 252 355 2 5 L 5 362 -367 7 85 79 0 254 262 7 187 161 10 122 -134 0 260 -348 5 104 -98 3 252 -274 2 258 -282 8 17 -12e -257 7 85 79 0 254 262 7 187 161 10 122 -134 0 260 -348 5 104 -98 3 252 -274 2 258 -282 8 17 -12e 1 377 324 8 34 2e 1 38 -35 6 48 -42 4 58 8 3 3 119 -96 9 30 111e 2 255 -261 9 49 41 1 2 255 -261 9 49 41	6	169 187	4 41 5 285 -3	27 117	-4.5 L	1 176 164 2 64 54	-6 6 L	1 191 192 2 46 -38	2 76 7C 3 31 9+	7 151 -146
-3 4 L	10	283 -284	6 70 7 92 -	70 <b>C</b>	161 -168 242 247	4 2CL -194	1 118 111	4 153 -155	5 31 -11+	9 121 194
C 365 355	••			31 3	25 -12* 288 301	6 128 121	3 253 -277 4 170 162	6 88 80	7 160 -147	-6 8 L 2 31 18*
2 19 278 1 276 -257 7 85 79 0 254 262 7 187 167 10 122 -134 0 380 -348 5 104 -98 3 252 -274 2 259 -262 E 179 -165 1 327 324 0 34 28 1 38 -35 6 48 -42 4 58 63 3 119 -96 9 30 114 2 255 -261 9 49 41 2 2160 183 7 62 54		365 355 303 300	£ 240 3	57 5	362 -367	4 6 1	5 36 -1* 6 367 -37*	£ 13C 134 9 287 287	2 & L	3 53 58 4 31 -64
4 58 63 3 119 -96 9 30 114 2 255 -261 9 49 41 2 180 183 7 62 54 5 373 366		19 27* 252 -274	1 276 -2 2 298 -2	57 7 162 E	85 79 179 -185	0 294 262 1 327 324	7 187 167 8 34 24	10 122 -134	0 380 -348 1 38 -35	6 48 -42
	5		3 119 -	96 9		2 255 -261	10 39 -38		2 180 183	r 62 54

Table 4. Continued.

9	24 -2C* 86 -94	1 9 L C 19 -9*	3 S L 0 136 -113	5 S L 0 132 110	7 29 22* 8 23 16*	3 159 -158 4 127 127 5 308 318	-5 9 L 1 61 -61	-7 9 L 3 151 163
	-7 8 L	1 280 -306	1 163 -157	1 234 240	-2 S L	6 70 <b>61</b>	2 104 87	4 40 -39
4	52 5C	2 154 145	2 35 16+	2 40 -41	0 267 277	7 187 -193	3 23 -37	5 108 -116
5	33 -24	3 115 106	3 165 164	3 153 -159	1 140 -121	E 61 -60	4 23 -29	6 54 67
6	26 2*	4 180 -178	4 47 -53		2 288 -268	9 18 -14*	5 199 -183	
7	24 12+	5 71 -70	5 25 -194	6 9 L	2 224 373	, ,,	6 23 37	
	105 -136	6 28 29	6 74 76	0 84 76			7 240 251	
٠	162 -130	7 56 60	0 /4 /0	1 51 -45		-4 9 L	£ 75 -75	
	0 9 L	. 50 00	4 9 L	2 39 -46	5 35 -37 6 58 -60	C 224 242 1 45 42	. 17 -19	
ı	270 222	2 9 L	C 224 -242		7 202 -209	2 88 -84	-6 5 L	
2	75 62	C 25C -277	1 55 -55	-1 9 L	8 42 43	3 39 -27	2 75 73	
3	305 - 324	1 273 -264	2 187 203	0 19 9*	9 89 99	4 69 -57	3 31 3+	
4	57 46	2 150 140	3 143 137	1 452 411		5 100 -103	4 31 -6*	
5	129 121	3 98 88	4 72 -74	2 32 -29	-3 9 L	6 34 5*	5 68 -70	
- 2	148 -129	4 61 -63	5 150 -175	3 144 -136	C 121 113	7 229 233	6 42 -39	
Š	105 -52	5 162 154	3 150 -175	4 147 147				
		6 134 125		5 124 -106	1 54 52	8 55 50		
8	77 74	7 33 -39			2 226 -239	9 185 205	E 22 -28	
				6 125 + 122				

 $F_{\rm c}$  values are compared with the  $F_{\rm o}$  values in Table 4. The atomic scattering factors of Doyle and Turner <sup>12</sup> were used, and the structure factors were weighted according to the formula  $w=(a+cF_{\rm o}{}^2+dF_{\rm o}{}^3)^{-1}$ , a satisfactory weight analysis being obtained with a=6.0, c=0.03, and d=0.001.

All calculations were performed on an IBM 360/65 computer. The absorption and extinction corrections were calculated with the programs DATAP2 and EXTCORR, the Fourier summations with DRF, and the least squares refinement with the full matrix program LALS. (The program system will be described elsewhere.<sup>18</sup>)

## HYDROGEN ATOM POSITIONS

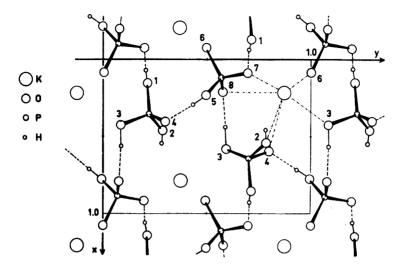
A final difference electron density summation was calculated using the parameters of Table 3. There are 20 hydrogen atoms in the unit cell, but the summation revealed as many as twelve four-fold positions corresponding to electron densities between 0.8 and 1.05 e/ų. However, eight of the peaks could be discounted, since they were situated too close to the potassium and phosphorus atoms. The four remaining peaks were considered as representing possible hydrogen atom sites. No peaks corresponding to the four remaining hydrogen atoms in the cell could, however, be detected. The positional parameters of the four hydrogen sites are given in Table 5.

Table 5. Hydrogen positions obtained in the final difference electron density calculation (the hydrogen atoms are numbered in accordance with the adjacent oxygen atom).

	x/a	y/b	z/c	$e/{ m \AA}^{3}$
$\mathbf{H}_{1}$	0.066	0.206	0.155	0.83
Η,	0.546	0.282	0.074	0.94
$\mathbf{H_{a}}^{T}$	0.559	0.088	0.284	0.83
$egin{array}{c} \mathbf{H_1} \\ \mathbf{H_2} \\ \mathbf{H_3} \\ \mathbf{H_5} \end{array}$	0.284	0.433	0.361	0.88

### DISCUSSION

The crystal structure of potassium orthophosphate, KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>, is built up from discrete phosphate tetrahedra, connected by hydrogen bonds and through the electrostatic action of the potassium ions. Well-defined sheets



containing 3/5 of the hydrogen bonds and the major part of the K-O interactions run perpendicular to the c axis throughout the structure (cf. Fig. 1). Apart from van der Waals forces, these sheets are held together by hydrogen bonds and weak electrostatic forces (cf. Fig. 2).

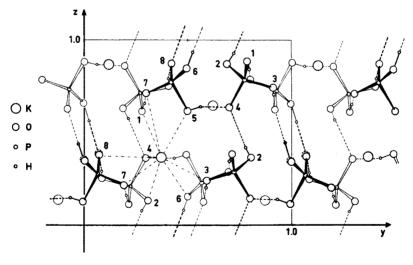


Fig. 2. A projection along the a axis. Phosphate groups having 0.5 < x < 1.0 have been drawn with full lines. Hydrogen bonds and K-O interaction are indicated as in Fig. 1.

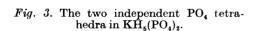
Within the two independent phosphate ions, the P-O distances range from 1.490 Å to 1.560 Å with a mean value of 1.530 Å. This value is slightly shorter than the mean value of 1.55 Å calculated for fourteen different monophosphates, reviewed by Liebau. This is, however, not unreasonable, since the influence of the hydrogen bonds on the P-O bonds is different in different phosphates, as already pointed out, for example by Jones and Cruickshank.

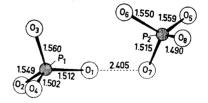
Since the expected bond length for a single P-O bond, as calculated from the normal covalent radii, is  $1.71~\text{\AA},^{14}$  it is generally accepted that  $\pi$  bonds are formed between the  $2p_{\rm O}$  and the  $3d_{\rm P}$  orbitals. The conditions necessary for the formation of such  $p_{\pi}-d_{\pi}$  bonds in phosphorus compounds have been extensively discussed by Hudson, 15 and according to his study, a P-O bond distance of 1.53 Å should correspond to an approximate  $\pi$  bond order of 0.5 Å.

Four of the eight different P-O bond distances in  $KH_5(PO_4)_2$  are significantly longer than the others (cf. Table 6 and Fig. 3). The corresponding

Table 6. Distances (Å) and angles (°) in the phosphate ion,  $H_5(PO_4)_2$  (standard deviations in parentheses).

$\begin{array}{c} P_1 - O_1 \\ P_1 - O_2 \\ P_1 - O_3 \\ P_1 - O_4 \end{array}$	1.512 (4) 1.549 (4) 1.560 (4) 1.502 (4)	$P_2 - O_5$ $P_2 - O_4$ $P_3 - O_7$ $P_2 - O_8$	1.559 (4) 1.550 (5) 1.515 (4) 1.490 (4)
$\begin{array}{c} O_1 - P_1 - O_2 \\ O_1 - P_1 - O_3 \\ O_1 - P_1 - O_4 \\ O_2 - P_1 - O_3 \\ O_2 - P_1 - O_4 \\ O_3 - P_1 - O_4 \end{array}$	110.6 (2) 105.7 (2) 115.7 (2) 107.6 (2) 105.9 (2) 111.0 (2)	$\begin{array}{c} O_5 - P_2 - O_6 \\ O_5 - P_2 - O_7 \\ O_5 - P_3 - O_8 \\ O_6 - P_2 - O_7 \\ O_6 - P_2 - O_8 \\ O_7 - P_3 - O_8 \end{array}$	105.6 (3) 104.4 (2) 112.6 (3) 109.0 (2) 112.4 (2) 112.3 (2)
$ O_1 - O_2 \\ O_1 - O_3 \\ O_1 - O_4 \\ O_2 - O_3 \\ O_2 - O_4 \\ O_3 - O_4 $	2.517 (5) 2.449 (6) 2.553 (5) 2.509 (5) 2.585 (5) 2.524 (6)	$ O_{6} - O_{6} \\ O_{5} - O_{7} \\ O_{5} - O_{8} \\ O_{6} - O_{7} \\ O_{6} - O_{8} \\ O_{7} - O_{8} $	2.476 (6) 2.429 (6) 2.537 (6) 2.496 (6) 2.527 (6) 2.495 (6)





oxygen atoms,  $O_2$ ,  $O_3$ ,  $O_5$ , and  $O_6$ , can therefore be considered to belong to hydroxyl groups. The P-OH bond distances in  $KH_5(PO_4)_2$  of 1.549-1.560 Å (mean value 1.555 Å) are in close agreement with the results found in

 $\rm H_3PO_4\cdot ^1_2H_2O^5$  with six independent P-OH distances of 1.542-1.561 Å and in  $\rm N_2H_5H_2PO_4$  and  $\rm N_2H_6(H_2PO_4)_2$  with corresponding distances of 1.550-1.573 Å. The P-OH bonds reported in  $\rm H_3PO_4$  (1.56<sub>8</sub>-1.57, Å), and in CaHPO<sub>4</sub> and Ca( $\rm H_2PO_4$ )<sub>2</sub>· $\rm H_2O$  (1.57<sub>6</sub>-1.62<sub>3</sub> Å) are not significantly longer than these in  $\rm KH_5(PO_4)_2$ , since the accuracy of these distances is approximately +0.02 Å.

Further support that  $O_2$ ,  $O_3$ , and  $O_5$  represent hydroxyl groups is provided by the positions indicated for the adjacent hydrogen atoms, since these yield probable O-H distances (cf. Table 5). In the neighbourhood of  $O_6$ , no definite hydrogen peak could be detected in the final difference electron density maps, but since only four of the five hydrogen atoms in the structure have been identified, it is reasonable to assume that the missing one is situated close to  $O_6$ .

Among the four shorter P-O bond distances it can only be stated, that  $P_2-O_8$  is significantly shorter than  $P_1-O_1$  and  $P_2-O_7$  (cf. Table 6), and, hence,  $O_8$  should correspond to a "keto" oxygen. It is not possible to decide on which of the remaining three oxygen atoms the fifth hydrogen atom is situated in terms of the P-O bond distances alone. However, there were indications in the final  $(F_o-F_c)$  maps that it might be attached to  $O_1$ . The mean "keto" P-O bond distance in  $KH_5(PO_4)_2$  would then be 1.502 Å (calculated for  $O_4$ ,  $O_7$ , and  $O_8$ ) which is in good agreement with the corresponding values found in other monophosphates, for example in  $N_2H_5H_2PO_4$  (1.505 Å), in  $N_2H_6(H_2PO_4)_2$  (1.509 Å), and in  $H_3PO_4\cdot\frac{1}{2}H_2O$  (1.490 Å).

The localisation of the hydrogen atoms based on the  $\dot{P}-O$  bond distances and indications in the difference electron density maps, is in good agreement with the hydrogen bond net which can be deduced from the short intermolecular O-O distances. The existence of five such distances below 2.65 Å indicates where each hydrogen bond ought to be situated, since the next shortest intermolecular O-O distance is as long as 3.307 Å. The most probable arrangement of the hydrogen bonds is given in Table 7 (cf. also Figs. 1 and 2). How-

Table 7. Distances (Å) and angles (°) describing the hydrogen bonds in  $KH_5(PO_4)_2$  (standard deviations in parentheses).

	O-H	$\mathbf{O} \cdots \mathbf{H}$	0-0	$\angle P - O - H$	∠0-H···0
$P_1 - O_1 - H_1 \cdots O_n$	0.90	1.51	2.405 (5)	118.4	174
$P_1 - O_2 - H_2 \cdots O_4$	0.99	2.09	2.585 (5)	149.8	108
$P_1 - O_3 - H_3 \cdots O_8$	0.97	1.68	2.636(5)	108.6	170
$P_2 - O_5 - H_5 \cdots O_4$	0.88	1.72	2.587 (6)	111.0	170
$P_a - O_a - H_a \cdot \cdot \cdot O_a$			2.596(5)		

ever, although  $H_1$  is found to be close to  $O_1$ , it is tempting to suggest that the extremely short  $O_1 - O_7$  distance of 2.405(5) Å corresponds to a symmetrical hydrogen bond. In view of the fact that the determination of the hydrogen atom positions is rather uncertain, the location of  $H_1$  alone ought not to exclude the possibility of a symmetrical hydrogen bond between  $O_1$  and  $O_7$ . The existence of such a bond is also supported by the distances  $P_1 - O_1$  and

 $P_2-O_7$ , which are approximately the same, and both significantly shorter than pure P-OH bonds. They are also slightly longer than the pure "keto" bonds, although both  $O_4$  and  $O_8$  serve as acceptors in two hydrogen bonds (cf. Table 7).

However, in spite of the fact that the  $O_1-O_7$  hydrogen bond is one of the shortest ever found (cf. e.g., Structural Inorganic Chemistry by Wells <sup>16</sup> or review articles by Bline and Hadzi <sup>17</sup> and Hamilton <sup>18</sup>), this fact alone cannot provide proof for a symmetrical hydrogen bond, since no simple relationship between the hydrogen bond type and the corresponding O-O distance has been found. <sup>17</sup> Further information could probably be obtained from a neutron diffraction investigation, which will be commenced in the near future.

On the average, the hydrogen bonds are strong in KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>, which is in accordance with the results reported for many other similar phosphorus compounds (cf. Table 8).

Table 8. Hydrogen bond distances in some phosphorus compounds.

Compound	Ref.	$O - H \cdots O$	Average
$H_3PO_3$	19	2.525, 2.545, 2.592, 2.599	2.565
LiH,PO,	20	2.567	2.567
KH,PO,	$\overline{21}$	2.487	2.487
Tetr., room temp.			
KH,PO,	22	2.486	2.486
Orth., at 77°K			
KH <sub>2</sub> PO <sub>4</sub>	23	2.51	2.51
Orth., at 116°K			
$NH_4H_2PO_4$	24	2.48	2.48
CaHPO <sub>4</sub>	6	2.44, 2.65, 2.58	2.56
$Ca(H_2PO_4)_2 \cdot H_2O$	6	2.48, 2.58, 2.60, 2.67, 2.72, 2.74	2.63
$N_2H_5H_2PO_4$	7	$2.555,\ 2.515$	2.535
$N_2H_6(H_2PO_4)_2$	8	$2.642,\ 2.612$	2.627
$KH_5(PO_4)_2$	Present	2.405, 2.585, 2.587, 2.636	2.553
	$\mathbf{work}$		
$H_3PO_4 \cdot \frac{1}{2}H_2O$	5	2.55, 2.58, 2.62	2.58
$H_3PO_4$	4	2.53, 2.53	2.53

Table 9. Distances (Å) less than 3.5 Å in the K-O polyhedron. The notation is in accordance with Figs. 1 and 2 (standard deviations in parentheses).

$K - O_1$	2.996 (4)	$K - O_a$	2.890 (4)
$\mathbf{K} - \mathbf{O}_{2}$	2.816(4)	$\mathbf{K} - \mathbf{O}_{\mathbf{z}}^{\circ}$	2.770(4)
$K - O_3$	2.750(4)	$\mathbf{K} - \mathbf{O}_{7}$	3.226(4)
$K - O_4$	3.138 (4)	$K - O_s$	3.210(5)
K = 0.	2.874 (4)	ŭ	, ,

The coordination of the potassium ion is ninefold (cf. Table 9) and irregular. The average K-O interaction distance is 2.963 Å which seems reasonable in comparison with the values reported in the *International Tables* (2.96 Å).<sup>25</sup>

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