

The Crystal Structures of Iron(III) and Potassium Dihydrogen Triphosphate *

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The crystal structures of $\text{FeH}_2\text{P}_3\text{O}_{10}$ and $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ have been determined from three-dimensional X-ray diffraction data. The iron salt is monoclinic, space group No. 14: $P2_1/c$, with $a=7.381(2)$, $b=8.808(4)$, $c=12.399(3)$ Å, $\beta=112.68(2)^\circ$ and $Z=4$. The potassium salt has an orthorhombic unit cell, space group No. 61: $Pbca$, with $a=7.588(2)$, $b=11.163(4)$ and $c=26.697(8)$ Å; $Z=8$. The structures contain discrete $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ groups held together by the metal ions and by hydrogen bonds. The bonding of the metal ions to the triphosphate group is discussed.

More than sixty hydrated and anhydrous acidic triphosphates of mono- and polyvalent metals have been described in the literature,^{1–3} but only for a few of them have crystal structure determinations been done: $\text{HZn}_2\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$,⁴ $\text{AlNH}_4\text{HP}_3\text{O}_{10}$,⁵ $\text{H}_2\text{FeP}_3\text{O}_{10} \cdot \text{H}_2\text{O}$,⁶ $\text{Co}(\text{NH}_3)_4\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$,⁷ $\text{HPb}_2\text{P}_3\text{O}_{10}$ ⁸ and $\text{YbH}_2\text{P}_3\text{O}_{10}$.⁹ In the present paper the structures of the compounds $\text{FeH}_2\text{P}_3\text{O}_{10}$ and $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ are reported as part of an investigation of the bonding of different metal ions to the triphosphate group.

Two types of acidic triphosphates with trivalent metal ions, $\text{H}_2\text{M}(\text{III})\text{P}_3\text{O}_{10}$, are known: MTPP–I and MTPP–II, where $\text{M}(\text{III})=\text{Al}$, Ga , V , Cr , Fe .^{10–15} MTPP–I can absorb water reversibly up

to a composition corresponding to a dihydrate $\text{H}_2\text{M}(\text{III})\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, and has ion-exchanging properties, in contrast to MTPP–II in which ion-exchange does not seem to take place.¹⁶ A complete structure determination has been reported for the iron salt $\text{FeH}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$, which has a layer structure with water molecules and metal ions between the layers.⁶ The octahedrally coordinated iron atom is bonded only to oxygens belonging to the triphosphate groups. The ion-exchange properties result from the layer structure of FeTPP–I and the mobility of its protons, which are in dynamic equilibrium with water molecules: $\equiv\text{POH} + \text{HOH} \rightleftharpoons \equiv\text{PO}^- + \text{H}_3\text{O}^+$.¹⁶ The difference in properties between MTPP–I and MTPP–II must be structurally related and it is of interest, therefore, to determine also the structure of one of the isomorphous compounds of the type $\text{M}(\text{III})\text{H}_2\text{P}_3\text{O}_{10}$ –II. We have chosen the iron salt $\text{FeH}_2\text{P}_3\text{O}_{10}$ for such a structure determination in order to facilitate a comparison with the already known structure of $\text{H}_2\text{FeP}_3\text{O}_{10} \cdot \text{H}_2\text{O}$.⁶

Several potassium triphosphates have been described in the literature: $\text{K}_5\text{P}_3\text{O}_{10}$, α - and β - $\text{K}_5\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, $\text{K}_5\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ and $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$,² as well as $\text{K}_2\text{H}_3\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$.¹⁷ It has been suggested that they can be used as components in fertilizers and the potassium dihydrogen triphosphate has become an object of study during the last few years since the rate of its degradation is comparable to that of $\text{K}_5\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ and it can exchange its hydrogens for ammonium to give a double salt $\text{K}_3(\text{NH}_4)_2\text{P}_3\text{O}_{10} \cdot n\text{H}_2\text{O}$.^{18,19} The potassium dihydrogen triphosphate was first prepared by Dewald.²⁰ Studies of

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its thermal stability in vacuum and in an atmosphere of water vapor and under mechanical treatment have been carried out.²¹⁻²³ An infra-red investigation of $K_3H_2P_3O_{10} \cdot H_2O$ has also been done recently.¹⁹

EXPERIMENTAL

Sample preparation. Single crystals of $FeH_2P_3O_{10}$ -II were prepared after d'Yvoire.¹⁰ A powder of iron(III)oxide (Fisher Scient. Comp. No. 74201) was dissolved in hot (150–180 °C) phosphoric acid H_3PO_4 (Merck, Art. 573, *p.a.* $d=1.71$) to give a ratio Fe:P=1:10. The hot melt was placed in a furnace at a carefully controlled temperature of 240 ± 0.5 °C for about 200 h. Good rhomboid shaped crystals were then obtained by slow cooling of the furnace. The crystals were washed with water and alcohol and were dried over P_2O_5 . They were identified by chemical analysis, paper chromatography and powder diffractometry. Phosphorous and iron were determined colorimetrically,⁹ giving: P=29.7 %, Fe=18.1 % and H_2O (TG-

analysis)=6.4 %. Calculated values for $FeH_2P_3O_{10}$ are P=29.90 %, Fe=17.9 %, and H_2O =5.80 %. Paper chromatography showed that the triphosphate ion, P_3O_{10} , was the only phosphate ion present. A powder photograph taken in a Guinier focusing camera with CuK_α radiation showed agreement with the diffraction pattern reported by d'Yvoire¹⁰ for $FeH_2P_3O_{10}$ -II. The density of the crystals was determined by displacement in benzene to 2.72 g cm^{-3} .

For the preparation of crystals of $K_3H_2P_3O_{10} \cdot H_2O$ 1 g of $K_3P_3O_{10}$ was dissolved in 1 ml of cold water (5 °C). About 1.5 ml of cold acetic acid (Merck, *p.a.* 100 %) was added to the mixture, which was then kept at about 2 °C in a refrigerator. For about an hour cold methanol was slowly added, but the addition was interrupted before crystallization was initiated. After leaving the mixture for a few days at 2 °C crystals began to appear and could grow to a size of about 1 mm. By paper chromatography and powder diffraction they were shown to be identical with the monohydrate.²³

X-Ray diffraction data. Precession and Weissenberg photographs were used to determine

Table 1. Crystal and refinement data.

	$FeH_2P_3O_{10}$	$K_3H_2P_3O_{10} \cdot H_2O$
Unit cell: <i>a</i> (Å)	7.381(2)	7.588(2)
<i>b</i>	8.808(2)	11.163(4)
<i>c</i>	12.399(3)	26.697(8)
β	112.68(2)	
<i>V</i> (Å ³)	806.08	2261.5
δ_{calc} (g cm ⁻³)	2.78 (Z=4)	2.99 (Z=8)
μ (cm ⁻¹)	27.6	16.6
Crystal dimensions (mm)	0.15×0.10×0.10	0.27×0.27×0.08
Absences	<i>h</i> 0 <i>l</i> for <i>l</i> =2 <i>n</i> +1 0 <i>k</i> 0 for <i>k</i> =2 <i>n</i> +1	0 <i>kl</i> for <i>k</i> =2 <i>n</i> +1 <i>h</i> 0 <i>l</i> for <i>l</i> =2 <i>n</i> +1 <i>hk</i> 0 for <i>h</i> =2 <i>n</i> +1
Space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
Observed independent reflections	1705	1990
Observed independent reflections with $I > 1.96\sigma(I)$	1474	1524
max. 2θ (°)	55	50
$R = \sum F_o - F_c / \sum F_o $	0.034	0.051
<i>R</i> incl. unobs. refl.	0.042	0.067
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	0.067	0.078
R_w incl. unobs. refl.	0.070	0.083
$[\frac{\sum w F_o - F_c ^2}{N_o - N_v}]^{1/2}$	1.2	1.6

symmetry and initial values for the unit cell dimensions. Intensity data were collected in a Syntex P2₁ automatic four-circle diffractometer with MoK_α radiation ($\lambda=0.7107 \text{ \AA}$); ω -scanning was used with scan speeds variable from 0.49°/min to 29.3°/min. Accurate unit cell dimensions were calculated by a least squares procedure using angular parameters for 15 selected reflections. Four check reflections, measured after every 100th reflection, showed no systematic variation in their intensities. Semi-empirical absorption corrections were applied by using values for the variation in intensity of selected reflections when rotated around the diffraction vector.²⁴ The Syntex XTL program system²⁵ and the thermal ellipsoid plot program,²⁶ Ortep-II, were used for the calculations.

Structure determinations. Crystallographic data are summarized in Table 1. The structures were solved by direct methods. For each structure the MULTAN program²⁷ provided a solution which led to a Fourier map from which most of the atoms in the unit cell could be located. A series of difference maps then gave positions for all remaining atoms.

FeH₂P₃O₁₀: Isotropic least squares refinements in which $\sum w||F_o|-|F_c||^2$, with the weighting function $w^{-1}=\sigma^2(F_o)+(0.05 F_o)^2$, was minimized, led to an *R* value of 0.043 for the 1474 observed reflections. With anisotropic temperature parameters and anomalous dispersion corrections the *R* value was lowered to 0.034 (with unobserved reflections included 0.042). In the final refinement cycle all shifts were smaller than 1 % of the corresponding standard deviations and in the final difference map no peak was higher than 0.62 e Å⁻³. When the two H atoms, H1 and H2, were not included in the structure factor calculations their heights in the corresponding difference maps were 0.95 and 0.52 e Å⁻³, respectively.

K₃H₂P₃O₁₀·H₂O: A least squares refinement minimizing $\sum w||F_o|-|F_c||^2$, with the weighting factor $w^{-1}=\sigma^2(F_o)+(0.005 F_o)^2$ for $F_o>3.92 \cdot \sigma$ led to an *R* value of 0.055 when all non-hydrogen atoms were included with anisotropic temperature coefficients and with anomalous dispersion corrections.

From a difference map at this stage likely positions for the hydrogen atoms could be found among peaks 0.5 e Å⁻³ and higher. When these were included in the least squares refinement, with isotropic temperature factors, the final *R* factor became 0.051 and, with unobserved reflections included, 0.067. In the final refinement cycle all shifts in positional and thermal parameters, including those of the hydrogen atoms, were less than 1 % of the corresponding standard deviations. In a final difference map the highest

remaining peak was 0.79 e Å⁻³. The lists of structure factors and temperature factors are available from the authors (G.J.).

Table 2a. Final positional parameters for FeH₂P₃O₁₀. All atoms occupy position 4(e) in space group No. 14: P2₁/c.²⁸

	<i>x</i>	<i>y</i>	<i>z</i>
Fe	0.25244(8)	0.07285(7)	0.29415(5)
P1	0.14532(15)	0.10352(12)	0.86660(9)
P2	0.35420(16)	0.10272(12)	0.70783(9)
P3	0.71116(15)	0.12205(12)	0.47813(9)
O1	0.2702(5)	0.0337(4)	0.7972(3)
O2	0.2889(5)	0.0758(4)	0.9943(3)
O3	0.2368(5)	0.4845(4)	0.0901(3)
O4	0.0335(5)	-0.0062(4)	0.1608(3)
O5	0.1043(4)	0.2323(3)	0.3351(3)
O6	0.4936(4)	0.3519(4)	0.9253(2)
O7	0.2997(4)	0.2324(3)	0.1855(3)
O8	0.5680(4)	0.4331(4)	0.2507(3)
O9	0.7975(5)	0.4207(4)	0.1047(3)
O10	0.8277(5)	0.2598(4)	0.4611(3)
H1	0.279(9)	0.138(8)	0.036(6)
H2	0.800(15)	0.319(15)	0.403(9)

Table 2b. Final positional parameters for K₃H₂P₃O₁₀·H₂O. All atoms occupy position 8(c) in space group No. 61: Pbc_a.²⁸

	<i>x</i>	<i>y</i>	<i>z</i>
K1	0.26555(18)	0.49106(12)	0.46440(4)
K2	0.23377(18)	0.48551(12)	0.29244(5)
K3	0.36217(19)	0.02814(12)	0.12345(5)
P1	0.10309(20)	0.24207(13)	0.03964(6)
P2	0.09255(20)	0.24752(13)	0.20874(6)
P3	0.34193(21)	0.22198(13)	0.37708(5)
O1	0.0898(6)	0.3749(4)	0.0404(2)
O2	0.0620(6)	0.3778(4)	0.2133(2)
O3	0.2698(5)	0.2077(4)	0.1911(2)
O4	0.1955(6)	0.1341(4)	0.3794(2)
O5	0.2807(6)	0.1857(4)	0.0467(2)
O6	0.3076(6)	0.3521(4)	0.3794(1)
O7	0.0562(7)	0.1768(5)	0.2583(2)
O8	0.4458(6)	0.1896(4)	0.3264(2)
O9	0.4808(8)	0.1823(4)	0.4184(2)
O10	0.5239(8)	0.3144(5)	0.0092(2)
O11	0.4436(8)	0.4045(5)	0.1436(3)
H1	0.472(11)	0.198(8)	0.219(3)
H2	0.466(11)	0.228(8)	0.526(3)
H3	0.387(11)	0.323(8)	0.148(3)
H4	0.007(11)	0.389(8)	0.374(3)

DISCUSSION OF THE STRUCTURES

Final parameter values are given in Table 2. Selected interatomic distances and angles are listed in Table 3 and stereoscopic drawings of the unit cell contents and of the bonding in and around the triphosphate groups are shown in Figs. 1 and 2.

$\text{FeH}_2\text{P}_3\text{O}_{10}$: each iron atom is coordinated by six oxygen atoms from four different triphosphate groups. The coordination with two of them is bidentate (Fig. 1b) with one oxygen belonging

Table 3. Selected interatomic distances (Å) and angles (°).

$\text{FeH}_2\text{P}_3\text{O}_{10}$		$\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$	
Within the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ group			
P1-O1	1.606(4)	P1-O9	1.601(6)
P1-O2	1.548(3)	P1-O10	1.568(6)
P1-O4	1.499(4)	P1-O1	1.487(4)
P1-O5	1.497(3)	P1-O5	1.499(5)
P2-O1	1.585(3)	P3-O9	1.588(6)
P2-O3	1.579(3)	P3-O8	1.606(5)
P2-O7	1.503(3)	P3-O4	1.484(5)
P2-O8	1.492(4)	P3-O6	1.477(4)
P3-O3	1.606(4)	P2-O8	1.594(5)
P3-O10	1.548(4)	P2-O7	1.566(5)
P3-O6	1.500(4)	P2-O2	1.478(4)
P3-O9	1.496(3)	P2-O3	1.493(4)
P2-P1	2.932(2)	P3-P1	2.978(2)
P2-P3	2.933(1)	P3-P2	2.991(2)
O2-H1	0.77(7)	O10-H2	0.80(10)
O10-H2	0.85(11)	O7-H1	0.91(9)
P1-P2-P3	124.02(5)	P1-P3-P2	98.12(6)
P1-O1-P2	133.5(2)	P1-O9-P3	139.0(4)
P2-O3-P3	134.1(2)	P3-O8-P2	138.4(3)

Other distances (Å) in $\text{FeH}_2\text{P}_3\text{O}_{10}$ Around the Fe^{3+} ion

($\text{Fe}-\text{O} < 3.4$ Å; $\text{Fe}-\text{P} < 3.5$ Å)

Fe-O4	1.941(3)	Fe-P1	3.239(1)
Fe-O5	1.963(3)	Fe-P1	3.177(1)
Fe-O6	2.005(3)	Fe-P2	3.299(1)
Fe-O7	2.066(3)	Fe-P2	3.238(1)
Fe-O8	2.037(3)	Fe-P3	3.302(1)
Fe-O9	1.964(3)	Fe-P3	3.225(1)

Hydrogen bonding

O2-H1...O7	157(7)	O10-H2...O8	148(10)
O2-O7	2.716(5)	O10-O8	2.991(5)

Table 3. Continued.

Other distances in $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$

Around the K^+ ions ($\text{K}-\text{O} < 3.1$ Å; $\text{K}-\text{P} < 4.5$ Å)

K1-O1	2.749(4)	K1-P1	3.511(2)
K1-O1	2.784(4)		3.729(2)
K1-O4	2.791(4)		3.961(2)
K1-O5	2.954(4)		3.781(2)
K1-O6	2.767(4)	K1-P3	3.846(2)
K1-O9	3.092(6)		3.570(2)
K1-O10	2.783(6)		
K2-O2	2.758(4)	K2-P2	3.633(2)
K2-O2	2.770(5)		3.910(2)
K2-O4	2.903(4)		3.832(2)
K2-O6	2.815(4)		3.804(2)
K2-O7	2.816(5)	K2-P3	3.799(2)
K2-O8	2.806(5)		3.522(2)
K2-O11	2.929(7)		
K3-O1	2.825(4)	K3-P1	3.818(2)
K3-O2	2.984(4)		3.908(2)
K3-O3	2.788(4)	K3-P2	3.920(2)
K3-O4	2.793(5)		3.888(2)
K3-O5	2.771(4)	K3-P3	3.089(2)
K3-O11	2.753(6)		4.235(2)

Around the water molecule

O11-H3	1.01(9)	O11-K2	2.929(7)
O11-H4	0.70(9)	O11-K3	2.753(6)

Hydrogen bonding

O7-H1...O3	160(8)	O11-H3...O3	149(7)
O10-H2...O5	159(10)	O11-H4...O6	140(10)
O7-O3	2.581(7)	O11-O3	2.858(7)
O10-O5	2.544(7)	O11-O6	2.890(8)

to the central PO_4 tetrahedron and the other to one of the terminal tetrahedra in the P_3O_{10} chain. The octahedral arrangement around the Fe atom is not quite regular, the largest distance is 2.066(3) Å and the shortest is 1.941(3) Å (average value 1.996 Å).

Within the triphosphate group the average length of P-O bonds involving the bridging oxygens O1 and O3 is 1.594 Å, which does not differ from the value reported for $\text{H}_2\text{FeP}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ (1.596 Å).⁶ For the oxygens shared between a PO_4 tetrahedron and an FeO_6 octahedron P-O bond lengths vary between 1.492(4) and 1.503(4) Å, with an average value of 1.498 Å. In $\text{H}_2\text{FeP}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ the variation is between 1.494 and 1.518 Å with an average of 1.500 Å.⁶ For the remaining oxygen atoms in the triphosphate group, O2 and O10, which are OH groups

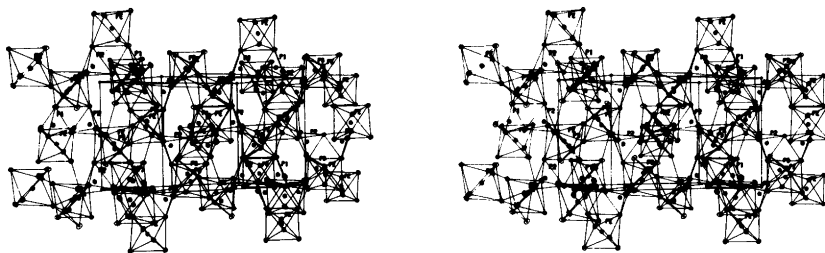


Fig. 1. a. The unit cell of $\text{FeH}_2\text{P}_3\text{O}_{10}$ viewed along the a axis with the c axis horizontal.

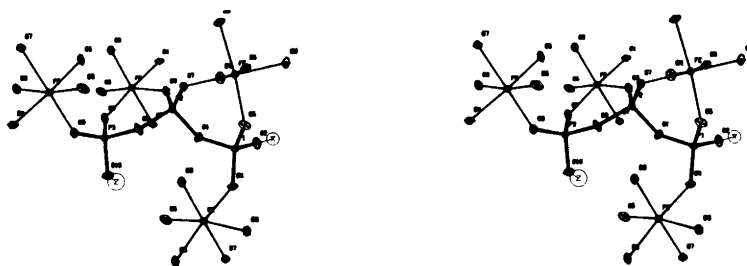


Fig. 1. b. A steric view of the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ group in $\text{FeH}_2\text{P}_3\text{O}_{10}$ with its coordinated FeO_6 octahedra.

according to the structure determination and are not coordinated to Fe, the corresponding P–O distances of 1.548(4) Å are, as expected, significantly longer than other P–O distances not involving the bridging oxygens. The H1 atom forms a hydrogen bond between O2 and O7 and

the H2 atom between O10 and O8, as judged from distances and angles involving these atoms (Table 3). This assignment is consistent with the significant lengthening of the Fe–O7 and the Fe–O8 bonds compared to other Fe–O bonds in the FeO_6 octahedron.

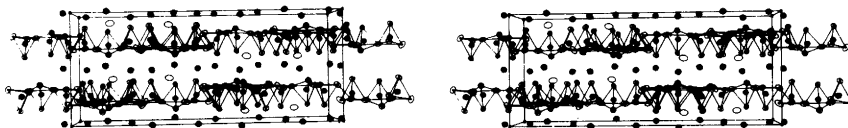


Fig. 2. a. The unit cell of $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ viewed along the b axis with the c axis horizontal.

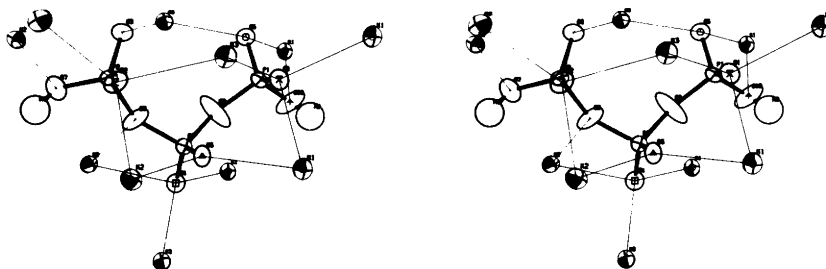


Fig. 2. b. A steric view of the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ group in $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ with surrounding potassium ions.

In $\text{H}_2\text{FeP}_3\text{O}_{10} \cdot \text{H}_2\text{O}$,⁶ the hydrogen atoms could not be located and there are no deviations for the P–O bonds corresponding to those of the P–O₂ and the P–O₁₀ bonds in the present structure. This would seem to be consistent with the previous observation¹⁶ that in the hydrated form the hydrogen atoms have a high mobility because of interaction with the water molecules: $\equiv\text{POH} + \text{HOH} = \equiv\text{PO}^- + \text{H}_3\text{O}^+$.

$\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$: within the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ groups the longest P–O bonds are those involving the bridging oxygens O8 and O9, with an average bond length of 1.597 Å (Table 3). One oxygen on each of the two terminal PO₄ groups is bonded to a hydrogen atom and the corresponding P–O bonds are 1.566(5) for P2–O7 and 1.568(6) Å for P1–O10. The remaining P–O bonds vary between 1.477(4) and 1.499(5) Å with an average value of 1.486 Å. These values do not differ significantly from those in $\text{FeH}_2\text{P}_3\text{O}_{10}$ (Table 3) or in crystal structures of other triphosphates.

Each of the three non-equivalent potassium ions is in close contact with six or seven oxygen atoms (Table 3). The bonding to the oxygens of the triphosphate group is shown in Fig. 2b. K1 and K2 each forms one bond to each of two different P₃O₁₀ groups and two bonds to each of two other P₃O₁₀ groups. K3 forms two bonds – one bond to each of the terminal PO₄ groups – to two P₃O₁₀ groups, and one bond to each of two other groups.

The two hydrogen atoms, H1 and H2, which belong to the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ group, form strong hydrogen bonds to oxygens in neighbouring triphosphate chains. This is indicated by the short distances O7–O3: 2.581(7) Å and O10–O5: 2.544(7) Å. The hydrogen bonds join the triphosphate groups into infinite sheets perpendicular to the *b* axis of the unit cell. All potassium ions are located between these sheets holding them together into a three-dimensional arrangement (Fig. 2). The water molecule, O11, forms two hydrogen bonds, both to oxygens within the P₃O₁₀ group: O11...O3: 2.858(7) Å and O11...O6: 2.890(8) Å. It is also in contact with two potassium ions: O11–K2 2.929(7) Å and O11–K3 2.753(6) Å, completing an approximately tetrahedral arrangement around it. The potassium ions seem to be rather spherically surrounded by phosphate groups as judged from the K–O(PO₄) and K–P distances (Table 3).

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