Structural Characterization of a Series of Cyclohexaphosphates: Ca$_2$M$_2$P$_6$O$_{18}$ · 6H$_2$O (*M* = K, Tl, Rb)

S. Abid and M. Rzaigui[1]

Laboratoire de Chimie des Matériaux, Faculté des Sciences, 7021 Zarzouna, Bizerte, Tunisia

Three new cyclohexaphosphates with the general formula Ca$_2$M$_2$P$_6$O$_{18}$ · 6H$_2$O (*M* = K, Tl, Rb) are reported. They crystallize with monoclinic unit cells and are isotopic. As an example the paramters of Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O are a = 7.266(1), b = 11.833(2), c = 12.300(2) Å, β = 103.17(1)°, Z = 2, P2$_1$/*n*, V = 1030(3) Å^3, and Dx = 2.387 g cm^{-3}. Crystal structure of this phase was determined using 6292 independent reflections with a final R = 0.025. The atomic arrangement can be described as puckered layers containing water bonded P$_6$O$_{18}$ anions and Ca^{2+} and K$^+$ cations, alternating along the (1, 0, 1) direction. Synthesis and characterization by X-ray diffraction, IR absorption, and TA are described.   © 1996 Academic Press, Inc.

INTRODUCTION

The study of the cyclohexaphosphates is of considerable importance as the P$_6$O$_{18}^{6-}$ anion in aqueous solution behaves as a polyelectrolyte, forming extraspherical complexes with cations thanks to electrostatic interactions (1). In the present investigation we report chemical preparation, characterization, and crystal structure of three Ca$_2$M$_2$ P$_6$O$_{18}$ · 6H$_2$O phases with *M* = K, Tl, and Rb. This work constitutes part of a more general investigation of divalent–monovalent cation cyclohexaphosphates.

EXPERIMENTAL

A. Chemical Preparation

Crystalline samples of the title compounds were prepared by slowly adding dilute cyclohexaphosphoric acid to an aqueous solution of calcium carbonate and alkaline carbonate with a stoichiometric ratio Ca/*M* = 1. Schematically, they react according to equation

$$2CaCO_3 + M_2CO_3 + H_6P_6O_{18}$$
$$+ 3H_2O \rightarrow Ca_2M_2P_6O_{18} \cdot 6H_2O + 3CO_2$$
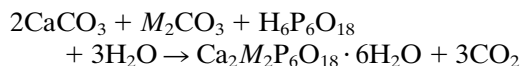
with *M* = K, Tl, and Rb.

[1] To whom correspondence should be addressed.

The cyclohexaphosphoric acid is added until pH 2 is reached in the final solution. After some days of slow evaporation at room temperature, crystals appeared with a suitable dimension. They were sparingly soluble in water and stable in air for months under normal conditions of temperature and hygrometry.

The cyclohexaphosphoric acid used in this reaction was prepared from an aqueous solution of Li$_6$P$_6$O$_{18}$ · 6H$_2$O (2) passed through an ion-exchange resin (Amberlite IR 120).

The compounds have been studied using different techniques with the experimental conditions described below.

B. Investigation

X-ray diffraction.   Powder diffraction patterns were recorded using a Philips PW 1729 diffractometer with the CuK$\bar{\alpha}$ radiation (λ = 1.5418 Å) and at low speed ($\frac{1}{8}$° θ/ min). The symmetry space group has been determined by Weissenberg technique on a single crystal. Unit cell parameters have been refined by a least square method using the powder data.

The intensity data collection was performed using a CAD4 Enraf–Nonius diffractometer. The strategy used for the structure determination and its final results are gathered in Table 1.

Thermal behavior.   Thermal analysis was performed using a multimodule 92 Setaram Analyzer operating from room temperature up to 873 K at an average heating rate of 10°/min.

Infrared spectroscopy.   Spectra were recorded in the range 4000–200 cm^{-1} with a Perkin–Elmer IR 983G spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

RESULTS AND DISCUSSION

A. Crystal Data

The Weissenberg and oscillation photographs show that the title compounds crystallize in the monoclinic P2$_1$/*n*

TABLE 1
Crystal Data and Experimental Parameters Used for the Intensity Data Collection; Strategy and Final Results of the Structure Determination

I. Crystal data

Formula: Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O	$Fw = 740.28$
Crystal system: monoclinic	Space group: $P2_1/n$
$a = 7.266 (1)$, $b = 11.833 (2)$,	$Z = 2$
$c = 12.300 (2)$ Å, $\beta = 103.17$ (1)°	$V = 1030(3)$ Å^3
Refinement of unit cell parameters with:	25 reflections (10.4° < θ < 11.6°)
$\rho_{cal.} = 2.387$ g cm^{-3}	$F(000) = 372$
Linear absorption factor:	$\mu(AgK\alpha) = 0.77$ mm^{-1}
Morphology: quadratic prism	Crystal size: 0.32 × 0.19 × 0.19 mm

II. Intensity measurements

Temperature: 294 K	Wavelength: AgKα (0.5608 Å)
Diffractometer: Enraf–Nonius CAD4	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Max scan time: 65 s	Theta range: 2–30
Measurement area: ±h, k, l	$h_{max.} = 12$, $k_{max.} = 20$, $l_{max.} = 21$
Total background measuring time:	$\frac{1}{2}$ scan time
Total number of scanned reflections:	6573
Total number of independent reflections:	6292
Two intensity and orientation reference reflections:	$\overline{2}71$, $2\overline{7}1$ (no variation)

III. Structure determination

Lorentz and polarization corrections	No absorption correction
Program used: MolEN (5)	Computer used: Micro-Vax 3100
Determination: Patterson and successive Fourier synthesis. H atoms from difference Fourier map.	
Thermal displacement parameters atoms: Isotropic for H atoms, anisotropic for other	
Unique reflections included:	3486 with $I > 4 \sigma(I)$
Weighting scheme: unitary	Refined parameters: 178
Residual Fourier density:	$-0.38 < \rho < 0.71$ e Å^{-3}
Unweighted agreement factor R:	0.025
Weighted agreement factor R_w:	0.027
e.s.d.: 0.86	Largest shift/error: 0.32

space group with the refined unit cell dimensions mentioned in Table 2. Indexing of the X-ray diffraction pattern, with the refined parameters, is reported for the three compounds in Table 3. The Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O unit cell parameters are close to those obtained with a four-circle diffractometer (Table 1).

B. IR Absorption Spectroscopy

The infrared absorption spectra exhibit:

—two broad bands at about 3600–3200 and another at 1650 cm^{-1} corresponding to the water molecules in the crystal arrangement, and

—various valency vibration bands the number and positions of which, between 1300 and 600 cm^{-1}, characterize a phosphoric ring anion (4). In this type of anions the vibrations of the O–P–O groups appear at relatively high frequencies, i.e., $1200 < \nu_{as} < 1300$ cm^{-1} and $1050 < \nu_s < 1200$ cm^{-1}. Those corresponding to the P–O–P groups give rise to a broad band ν_{as} around 960 cm^{-1} and a doublet ν_s between 800 and 700 cm^{-1}. Figure 1a shows, as an example, the IR spectrum of Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O.

C. Thermal Analysis

At rising temperature the compounds show similar transformations between 100 and 600°C (Table 4). We describe here the thermal behavior on hand of that of Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O.

Two curves corresponding to DTA and TGA analyses in open air are given in Fig. 2 for Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O. In order to prepare an interpretation as correct as possible of the two curves, we performed, in addition, an investigation by X-ray diffraction and IR absorption which we report and discuss below.

The thermal analysis curves show that the cyclohexaphosphate Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O undertakes at about 125 and 170°C two endothermic dehydrations well confirmed by

TABLE 2
Main Crystal Data for Ca$_2$M$_2$P$_6$O$_{18}$ · 6H$_2$O Cyclohexaphosphates

Compounds	Unit cell parameters			S.G.	Z	V (Å)
	a / α	b / β	c(Å) / γ(°)			
Ca$_2$K$_2$P$_6$O$_{18}$ · 6H$_2$O	7.309(3)	11.862(3) / 103.22(2)	12.335(3)	$P2_1/n$	2	1041
Ca$_2$Tl$_2$P$_6$O$_{18}$ · 6H$_2$O	7.233(3)	11.582(5) / 99.94(2)	12.193(4)	$P2_1/n$	2	1006
Ca$_2$Rb$_2$P$_6$O$_{18}$ · 6H$_2$O	7.290(3)	11.593(3) / 100.86(1)	12.236(3)	$P2_1/n$	2	1016
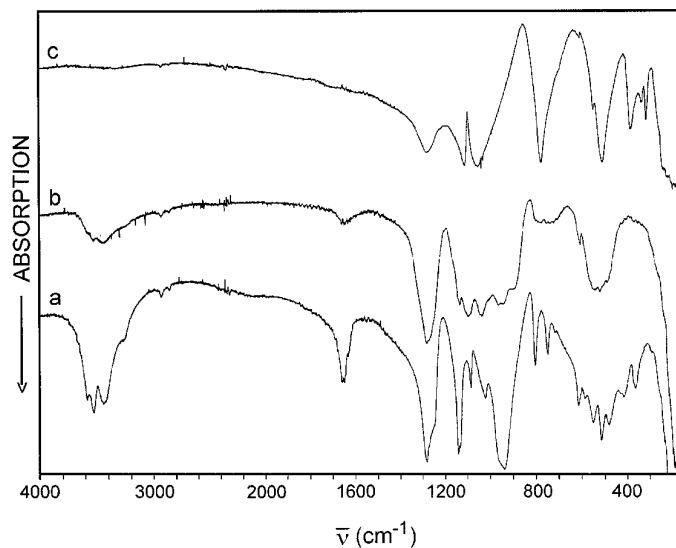
FIG. 1. IR spectra of the phosphates: (a) $Ca_2K_2P_6O_{18} \cdot 6H_2O$, (b) amorphous phase, and (c) anhydrous compound.

TABLE 4
Main Thermal Data for $Ca_2M_2P_6O_{18} \cdot 6H_2O$ Cyclohexaphosphates

Compounds	Thermal analyses Pics temperature (°C)			
$Ca_2K_2P_6O_{18} \cdot 6H_2O$	125	170	500	562
$Ca_2Tl_2P_6O_{18} \cdot 6H_2O$	139	196	485	544
$Ca_2Rb_2P_6O_{18} \cdot 6H_2O$	138	159	450	507

ray beam (Fig. 3b) and which no more exhibits the IR absorption bands characteristic of a cyclic phosphate (Fig. 1b). This amorphous phase itself dehydrates in turns in a wide temperature range, 230–550°C, to crystallize at 562°C (exothermic peak, Fig. 2) into an anhydrous compound the IR spectrum of which (Fig. 1c) characterizes a condensed phosphate with ring anions (4). The X-ray diffractogram of the crystallized phase (Fig. 3c) corresponds to that of the cyclotriphosphate $CaKP_3O_9$ identified elsewhere (5).

In conclusion, from the global TGA weight loss curve, we may deduce the presence of six water molecules per formula unit (% water: experimental 14.2, calculated 14.6), which the structural analysis by X-ray diffraction confirms clearly.

the weight losses observed on the TGA curve. According to the latter, a slight weight loss corresponds to a first dehydration. This partial dehydration leads to an intermediate amorphous phase which does not diffract the X-

TABLE 3
X-Ray Powder Diffraction Data for $Ca_2M_2P_6O_{18} \cdot 6H_2O$

			$Ca_2K_2P_6O_{18} \cdot 6H_2O$						$Ca_2Tl_2P_6O_{18} \cdot 6H_2O$						$Ca_2Rb_2P_6O_{18} \cdot 6H_2O$		
h	k	l	d_{cal} (Å)	d_{obs} (Å)	I(%)	h	k	l	d_{cal} (Å)	d_{obs} (Å)	I(%)	h	k	l	d_{cal} (Å)	d_{obs} (Å)	I(%)
0	1	1	8.44	8.44	100	0	1	1	8.34	8.34	100	0	1	1	8.34	8.35	100
1	1	0	6.10	6.10	4	1	1	0	6.07	6.07	10	$\bar{1}$	1	1	5.82	5.82	4
0	0	2	6.00	6.00	6	0	2	1	5.22	5.21	16	0	1	2	5.33	5.34	12
$\bar{1}$	1	1	5.93	5.93	8	$\bar{1}$	1	2	4.62	4.62	9	0	2	1	5.22	5.23	15
0	2	0	5.93			0	2	2	4.17	4.17	14	0	2	2	4.17	4.17	11
0	1	2	5.36	5.36	10	1	2	1	4.07	4.06	11	1	2	1	4.06	4.06	5
1	1	1	5.05	5.05	3	0	1	3	3.78	3.78	16	1	1	2	3.97	3.97	3
0	1	3	3.79	3.79	12	$\bar{1}$	0	3	3.78			0	1	3	3.79	3.79	14
0	3	1	3.76	3.76	12	2	1	0	3.40	3.40	18	2	1	0	3.42	3.42	40
$\bar{1}$	1	3	3.70	3.70	3	1	3	0	3.39	3.39	19	0	2	3	3.30	3.30	11
2	1	0	3.41	3.41	18	$\bar{1}$	3	1	3.34	3.34	16	0	3	2	3.25	3.25	58
0	3	2	3.30	3.30	18	0	2	3	3.29	3.29	13	1	1	3	3.13	3.12	8
$\bar{1}$	3	2	3.15	3.15	9	0	3	2	3.25	3.25	41	0	0	4	3.00	3.00	24
0	0	4	3.00	3.00	6	$\bar{1}$	2	3	3.17	3.17	7	0	4	0	2.898	2.900	17
0	4	0	2.966	2.966	7	1	1	3	3.14	3.13	11	$\bar{1}$	1	4	2.884	2.884	7
$\bar{2}$	2	2	2.965			0	0	4	3.00	3.00	14	1	2	3	2.832	2.831	6
0	1	4	2.910	2.911	8	0	1	4	2.907	2.906	9	0	3	3	2.781	2.781	20
0	4	1	2.879	2.879	4	$\bar{2}$	1	3	2.835	2.834	7	1	4	0	2.686	2.686	17
1	2	3	2.810	2.810	9	0	3	3	2.779	2.780	27	$\bar{2}$	2	3	2.637	2.636	10
$\bar{1}$	2	4	2.695	2.694	5	$\bar{1}$	3	3	2.701	2.701	6	0	4	2	2.610	2.611	9
$\bar{2}$	2	3	2.695			0	2	4	2.666	2.667	6	1	4	1	2.583	2.583	3
0	2	4	2.679	2.678	6	$\bar{1}$	2	4	2.632	2.632	7	$\bar{1}$	4	2	2.520	2.519	8
0	4	2	2.659	2.659	5	$\bar{2}$	2	3	2.610	2.610	9	$\bar{2}$	1	4	2.490	2.491	15
$\bar{1}$	4	2	2.578	2.578	4	1	1	4	2.547	2.547	7						
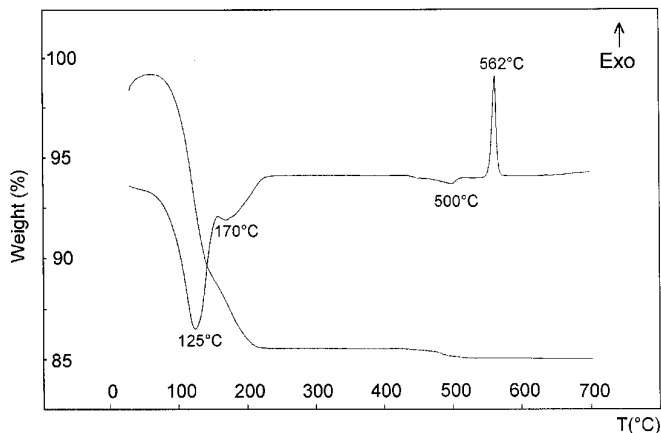
FIG. 2. DTA and TGA curves of $Ca_2K_2P_6O_{18} \cdot 6H_2O$ at rising temperature.

D. Structure Description

Final atomic coordinates of all atoms of Ca_2K_2 $P_6O_{18} \cdot 6H_2O$ and their B_{eq} are given in Table 5.[2] Figure 4 shows a perspective view of the corrugated layers in the $Ca_2K_2P_6O_{18} \cdot 6H_2O$ structure ($P2_1/n$).

The cyclohexaphosphate anions. The two P_6O_{18} ring anions are located around the inversion centers at (0, 0,

[2] List of structure factors and anisotropic thermal parameters are available on request to the authors.

TABLE 5
Final Atomic Coordinates and B_{eq} for the Nonhydrogen Atoms, B_{iso}, for H Atoms

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}(\sigma)$
Ca	0.42112(4)	0.28955(3)	0.29631(3)	0.961(4)
K	0.86954(6)	0.09537(4)	0.09455(4)	1.741(6)
P1	0.33202(6)	0.18064(4)	0.01894(3)	0.853(5)
P2	0.59319(6)	−0.01035(4)	−0.18662(3)	0.848(5)
P3	0.42217(6)	0.21005(4)	−0.19320(3)	0.858(5)
O(E11)	0.3130(2)	0.2737(1)	0.0960(1)	1.33(2)
O(E12)	0.6561(2)	0.3691(1)	0.4503(1)	1.21(2)
O(L12)	0.4616(2)	0.0822(1)	0.0869(1)	1.08(2)
O(E21)	0.0778(2)	0.5840(1)	0.2147(1)	1.37(2)
O(E22)	0.2277(2)	0.9494(1)	0.1405(1)	1.36(2)
O(L23)	0.9187(2)	0.4250(1)	0.2891(1)	1.27(2)
O(E31)	0.7707(2)	0.7485(1)	0.2420(1)	1.39(2)
O(E32)	0.0845(2)	0.2396(1)	0.2702(1)	1.41(2)
O(L31)	0.5310(2)	0.7806(1)	0.0587(1)	1.23(2)
O(W1)	0.4973(2)	0.4782(1)	0.2026(1)	2.24(3)
O(W2)	0.5954(2)	0.7983(1)	0.5095(1)	2.07(3)
O(W3)	0.7459(3)	0.5129(2)	0.0462(2)	2.78(3)
				B_{iso}
H(1W1)	0.075(6)	0.029(4)	0.305(3)	3(1)
H(2W1)	0.564(6)	0.478(4)	0.155(3)	3(1)
H(1W2)	0.484(6)	0.812(4)	0.461(3)	4(1)
H(2W2)	0.851(6)	0.352(4)	−0.001(3)	3(1)
H(1W3)	0.830(6)	0.545(4)	0.093(3)	4(1)
H(2W3)	0.286(7)	−0.977(4)	0.515(4)	6(1)

Note. e.s.d. are given in parentheses. $B_{eq} = \frac{4}{3} \sum_i \sum_j \mathbf{a}_i \mathbf{b}_j \beta_{ij}$.

FIG. 3. X-ray powder diffractograms of the phosphates: (a) Ca_2K_2 $P_6O_{18} \cdot 6H_2O$, (b) amorphous phase, and (c) anhydrous compound.
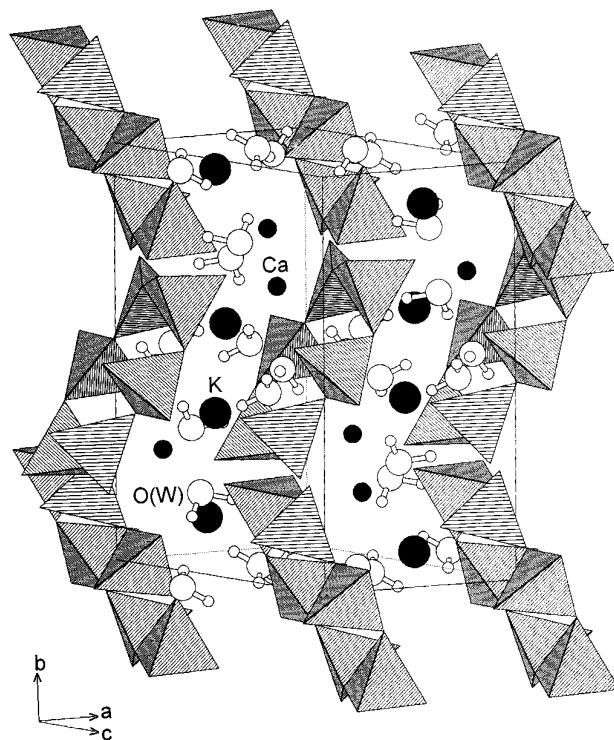
FIG. 4. Perspective view of the $Ca_2K_2P_6O_{18} \cdot 6H_2O$ structure.

TABLE 6
Main Interatomic Distances (Å) and Bond Angles (°) in
$Ca_2K_2P_6O_{18} \cdot 6H_2O$

The P(1)O$_4$ tetrahedron				
P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	<u>1.480(1)</u>	2.537(2)	2.523(2)	2.511(2)
O(E12)	117.72(8)	<u>1.484(1)</u>	2.526(1)	2.529(2)
O(L12)	109.58(7)	109.61(7)	<u>1.607(1)</u>	2.427(2)
O(L13)	109.35(8)	110.34(7)	98.54(7)	<u>1.596(1)</u>

The P(2)O$_4$ tetrahedron				
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	<u>1.477(1)</u>	2.560(2)	2.521(2)	2.488(2)
O(E22)	119.74(8)	<u>1.483(2)</u>	2.510(2)	2.534(2)
O(L12)	109.14(7)	108.19(7)	<u>1.615(1)</u>	2.437(2)
O(L23)	108.13(7)	110.79(7)	98.81(7)	<u>1.595(1)</u>

The P(3)O$_4$ tetrahedron				
P(3)	O(E31)	O(E32)	O(L32)	O(L13)
O(E31)	<u>1.477(1)</u>	2.553(2)	2.482(2)	2.543(2)
O(E32)	119.42(8)	<u>1.480(1)</u>	2.538(2)	2.484(2)
O(L23)	106.87(7)	110.29(8)	<u>1.612(1)</u>	2.450(2)
O(L13)	110.61(7)	106.61(7)	101.54(7)	<u>1.615(1)</u>
P(1)–P(2)	2.8457(6)	P(1)–O(L12)–P(2)		124.07(8)
P(1)–P(3)	2.8527(6)	P(1)–O(L13)–P(3)		125.36(7)
P(2)–P(3)	2.8819(6)	P(2)–O(L23)–P(3)		127.95(8)
	P(1)–P(2)–P(3)	132.14(2)		
	P(1)–P(3)–P(2)	92.94(2)		
	P(2)–P(1)–P(3)	134.72(2)		

The CaO$_8$ polyhedron			
Ca–O(E11)	2.416(1)	Ca–O(E13)	2.440(1)
Ca–O(E21)	2.436(1)	Ca–O(E23)	2.465(1)
Ca–O(E12)	2.432(1)	Ca–O(W1)	2.628(2)
Ca–O(E22)	2.395(1)	Ca–O(W2)	2.632(2)

The KO$_{11}$ polyhedron			
K–O(L12)	2.949(1)	K–O(E13)	3.049(1)
K–O(E12)	3.057(1)	K–O(E23)	2.913(1)
K–O(E12)	2.732(1)	K–O(L31)	3.418(1)
K–O(E22)	2.865(1)	K–O(W1)	2.825(2)
K–O(E22)	3.066(1)	K–O(W2)	2.760(2)
K–O(L23)	3.445(1)		

The hydrogen-bond				
O(W)–H $\cdots$ O	O(W)–H	H $\cdots$ O	O(W)–H $\cdots$ O	O(W)–O
O(W1)–H(1W1) $\cdots$ O(E23)	0.79(4)	2.53(4)	140(4)	3.181(2)
O(W1)–H(2W1) $\cdots$ O(W3)	0.84(4)	2.12(4)	168(4)	2.952(3)
O(W2)–H(1W2) $\cdots$ O(E11)	0.91(4)	2.16(4)	148(4)	2.970(2)
O(W2)–H(2W2) $\cdots$ O(W3)	0.77(4)	2.17(4)	169(3)	2.934(2)
O(W3)–H(1W3) $\cdots$ O(E21)	0.83(4)	2.12(4)	165(4)	2.923(2)
O(W3)–H(2W3) $\cdots$ O(W2)	0.68(5)	2.32(5)	150(5)	2.934(2)
	H(1W1)–O(W1)–H(2W1)	114(4)		
	H(1W2)–O(W2)–H(2W2)	99(4)		
	H(1W3)–O(W3)–H(2W3)	110(5)		

Note. e.s.d. vlaues are given in parentheses.

0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). In these centrosymmetrical P$_6$O$_{18}$ groups, the three P–P–P angles vary from 92.94° to 134.72°. This range is wider than that observed in (EDA)$_3$P$_6$O$_{18}$ · 2H$_2$O (6) with the same space group $P2_1/n$, in which the P–P–P angle varies from 91.76° to 111.90°. On the other hand, the local arrangement around one PO$_4$ tetrahedron and the P–O–P bond angles are quite similar to those normally observed in all other condensed phosphoric anions. Table 6 reports the main interatomic distances and bond angles in this P$_6$O$_{18}$ ring anion.

Cation environments.   Within a coordination sphere of 2.7 Å, the Ca atom has an eightfold coordination, resulting from six external oxygen atoms belonging to three P$_6$O$_{18}$ rings and two water molecules. The CaO$_8$ polyhedron is slightly distorted with Ca–O distances ranging between 2.395 and 2.632 Å (Table 6). The shortest Ca–Ca distance is 6.42 Å.

The potassium atom is coordinated, within a range of 3.5 Å, with eleven oxygen neighbors including two water molecules and nine external and internal oxygen atoms of the PO$_4$ tetrahedra. Each KO$_{11}$ polyhedron joins three P$_6$O$_{18}$ rings, while each anionic ring connects six K polyhedra and six Ca octahedra. The shortest K–K distance is 4.01 Å. The water molecules, O(W1) and O(W2), take part in the coordination polyhedra of the Ca and K atoms. The third water molecule O(W3) is connected by H bonds to O(E21) and O(W2). Figure 4 shows that the atomic arrangement can be considered as a succession of two types of corrugated layers stacked perpendicularly to the (1, 0, 1) direction. The first type of layer contains the centrosymmetrical phosphoric groups, and the second the water molecules and the K and Ca atoms. A three-dimensional network of hydrogen bonds connecting these two types of layers is described in Table 6.

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