



CHEMICAL PREPARATION, THERMAL BEHAVIOR AND CRYSTAL STRUCTURE OF CALCIUM-CESIUM CYCLOHEXAPHOSPHATE DIHYDRATE

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ABSTRACT

Chemical preparation and crystal structure are given for a new monovalent–divalent cation cyclohexaphosphate. This compound is monoclinic $P2_1/c$ with the following unit cell parameters: $a = 9.087(2)$, $b = 12.246(4)$, $c = 9.895(4)$ Å, $\beta = 116.98(2)^\circ$, $Z = 2$, $V = 981(1)$ Å³, and $D_x = 2.897$ g·cm⁻³. The atomic arrangement can be described as successive wide layers made by the P_6O_{18} ring anions and interconnected by the CaO_6 and CsO_8 polyhedra and the hydrogen bonds. Crystal structure was solved with a final R value of 0.032 for 6263 independent reflections. The thermal behavior has been investigated and interpreted by comparison with IR absorption spectroscopy and X-ray diffraction experiments.

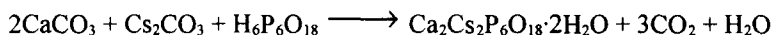
KEYWORDS: A. inorganic compounds, B. chemical synthesis, C. infrared spectroscopy, C. thermogravimetric analysis (TGA), C. X-ray diffraction

INTRODUCTION

Multivalent metal phosphates have a number of technologically useful properties (1). However, this has posed the question of industrial manufacture of a number of condensed phosphates, many of them being required in the form of perfect single crystals. We report in this work the chemical preparation, characterization and crystal structure of $Ca_2Cs_2P_6O_{18} \cdot 2H_2O$, a new cyclohexaphosphate of mixed monovalent–divalent cations.

EXPERIMENTAL

Chemical Preparation. Crystals of the title compound are prepared by slowly adding dilute cyclohexaphosphoric acid to an aqueous solution of calcium carbonate and cesium carbonate with a stoichiometric ratio $\text{Ca/Cs} = 1$, according to the following chemical reaction:



The so-obtained solution is then slowly evaporated at room temperature until large rectangular prisms of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$ are formed. These crystals are 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 $\text{Li}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ (2) passed through an ion-exchange resin (Amberlite IR 120).

The title compound has been studied through different techniques with experimental conditions described below.

Investigation.

X-ray diffraction. Powder diffraction patterns were registered with a Philips PW 1729 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and at low speed ($1/8^\circ/\text{min}$). The symmetry space group has been determined by the Weissenberg technique on a single crystal. Unit cell parameters have been refined by a least-squares 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 the multimodule 92 Setaram Analyzer operating from room temperature up to 773 K at an average heating rate of $10^\circ/\text{min}$.

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

RESULTS AND DISCUSSION

Crystal Data. The Weissenberg and oscillation photographs show that the title compound crystallizes in the monoclinic $\text{P2}_1/\text{c}$ with the refined unit cell dimensions $a = 9.103(5)$, $b = 12.264(5)$, $c = 9.908(4) \text{ \AA}$, and $\beta = 116.91(2)^\circ$. These values are comparable to those obtained with the four circle diffractometer data (Table 1). Indexing of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$ X-ray diffraction pattern with these unit cell parameters is reported in Table 2.

IR Absorption Spectroscopy. The infrared absorption spectrum of the title compound is reported in Figure 1a. It exhibits:

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

I. Crystal data	
Formula: $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$	Fw = 855.82
Crystal system: monoclinic	Space group: $\text{P}2_1/\text{c}$
$a = 9.087(2)$, $b = 12.246(4)$, $c = 9.895(4)$ Å, $\beta = 116.98(2)^\circ$	$Z = 2$ $V = 981(1)$ Å ³
Refinement of unit cell parameters with: $\rho_{\text{cal.}} = 2.897 \text{ g}\cdot\text{cm}^{-3}$	22 reflections ($11.4^\circ < \theta < 12^\circ$) $F(000) = 404$
Linear absorption factor:	$\mu(\text{AgK}\alpha) = 2.49 \text{ mm}^{-1}$
Morphology: rectangular prism	Crystal size: $0.25 \times 0.19 \times 0.18 \text{ mm}$
II. Intensity measurements	
Temperature: 294 K	Wavelength: $\text{AgK}\alpha$ (0.5608 Å)
Diffractometer: Enraf-Nonius CAD4	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Scan speed: $0.02^\circ \text{ s}^{-1}$	Theta range: 3–30
Measurement area: $\pm h, k, l$	$h_{\text{max}} = 14$, $k_{\text{max}} = 20$, $l_{\text{max}} = 17$
Total background measuring time:	1/2 scan time
Total number of scanned reflections:	6312
Total number of independent reflections:	6263
Two intensity and orientation reference reflections:	$4\bar{5}\bar{5}, 45\bar{5}$ (no variation)
III. Structure determination	
Lorentz and polarization corrections	No absorption correction
Program used: Molen (3)	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:	2861 with $I > 3 \sigma(I)$
Weighting scheme: unitary	Refined parameters: 144
Residual Fourier density:	$-1.903 < \rho < 1.093 \text{ e}\cdot\text{Å}^{-3}$
Unweighted agreement factor R:	0.037
Weighted agreement factor R_w :	0.039
Esd: 1.69	Largest shift/error: 0.23

- two broad bands at about $3600\text{--}3200 \text{ cm}^{-1}$ and another one at 1650 cm^{-1} corresponding to the water molecules of the arrangement.
- various valency vibration bands for which both positions, between 1300 and 600 cm^{-1} , and number are typical of a phosphoric ring anion (4). In this type of anions the vibrations of the $\text{O}^-\text{P}\text{--}\text{O}^-$ groups take place at relatively high frequencies, $1200 < \nu_{\text{as}} < 1300 \text{ cm}^{-1}$ and $1050 < \nu_{\text{s}} < 1200 \text{ cm}^{-1}$ and those corresponding to the P–O–P groups appear as a broad band ν_{as} around 960 cm^{-1} and a doublet ν_{s} between 800 and 700 cm^{-1} .

Thermal Analysis. The two curves corresponding to the DTA and TGA analyses in air atmosphere of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$ are given in Figure 2. In order to interpret these two

TABLE 2
X-ray Powder Diffraction Data for $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$

h k l	$d_{\text{cal.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	I/I_{max}	h k l	$d_{\text{cal.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	I/I_{max}
1 0 0	8.12	8.12	9	0 4 0	3.06	3.06	6
0 2 0	6.13	6.13	4	-2 3 1	3.04	3.04	10
-1 0 2	4.93	4.93	38	0 3 2	3.00	3.00	16
-1 2 2	3.84	3.84	56	-3 1 2	2.902	2.902	12
0 3 1	3.71	3.71	15	1 4 0	2.868	2.870	5
1 3 0	3.65	3.65	100	-2 3 2	2.871		
-2 2 1	3.65			0 4 2	2.519	2.519	6
0 2 2	3.58	3.58	10	-2 0 4	2.464	2.464	4
-2 2 2	3.37	3.37	3	-3 2 3	2.463		
1 0 2	3.30	3.30	9	-1 0 4	2.428	2.427	7
1 1 2	3.19	3.19	9	-1 1 4	2.382	2.382	5
1 3 1	3.15	3.15	7				

diagrams as properly as possible, we performed, in addition, a study by X-ray diffraction and IR absorption, which we report and discuss below.

The thermal analysis curves show that the cyclohexaphosphate $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$ undertakes at about 280 and 382 °C two endothermic dehydrations well confirmed by the

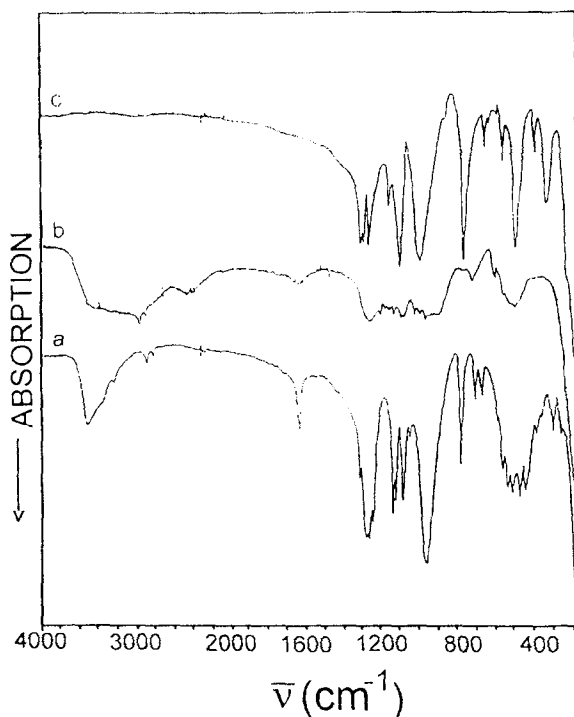


FIG. 1

IR spectra of the phosphates: (a) $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$, (b) amorphous phase, and (c) anhydrous compound.

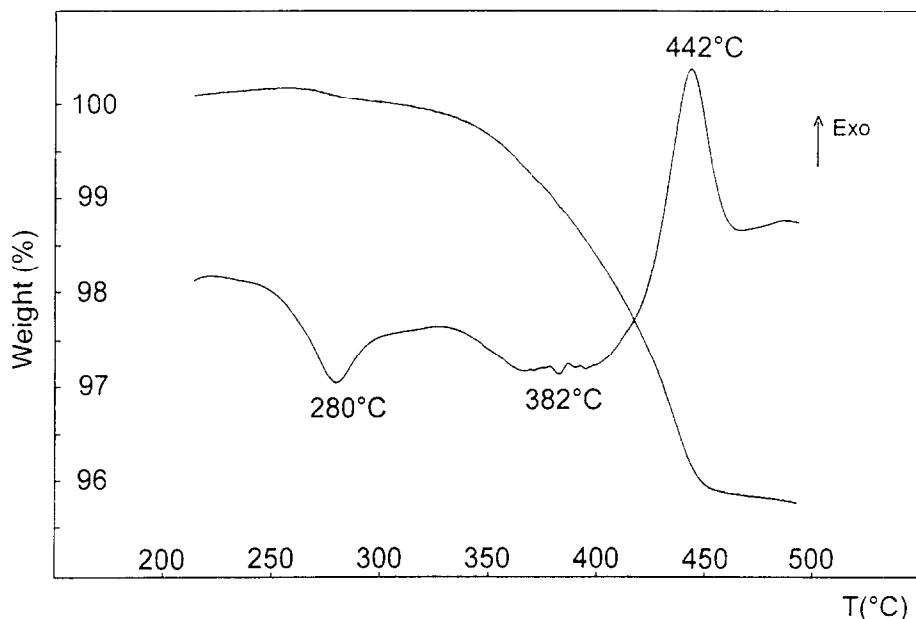


FIG. 2
DTA, TGA, and DTG curves of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$.

weight losses observed on the TGA curve. According to the latter, a slight weight loss corresponds to the first dehydration. This partial dehydration brings to an intermediate amorphous phase which does not diffract the X-ray (Fig. 3b) and no longer exhibits the IR absorption bands characteristic of a cyclic phosphate (Fig. 1b).

This amorphous phase itself dehydrates in a wide temperature range of 325–430 °C to crystallize at 442 °C (exothermic peak Fig. 2) into an anhydrous compound, the IR spectrum (Fig. 1c) of which is characteristic of condensed phosphates with ring anions (4). The X-ray diffractogram of the crystallized compound (Fig. 3c) corresponds to that of the cyclotriphosphate CaCsP_3O_9 , identified elsewhere (5).

In conclusion, from the global TGA weight loss curve, we deduce two water molecules per formula unit (% water: experimental 4.3, calculated 4.2), which the structural analysis by X-ray diffraction confirms.

Structure Description. Final atomic coordinates of all atoms and their B_{eq} are given in Table 3 and the anisotropic thermal parameters in Table 4. Figure 4 represents the projection of the atomic arrangement along the \vec{a} axis. Main geometrical features, bond distances, and angles in this arrangement are reported in Table 5.

Figure 4 shows that the basic structural units of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot\text{H}_2\text{O}$ are six-membered rings of PO_4 tetrahedra joined at the vertices, water molecule, calcium and cesium cations. In the plane parallel to (\vec{a}, \vec{c}) , the P_6O_{18} rings are connected by the calcium octahedra, forming an open-work layer. The water molecule and cesium atom are located in the interlayer space.

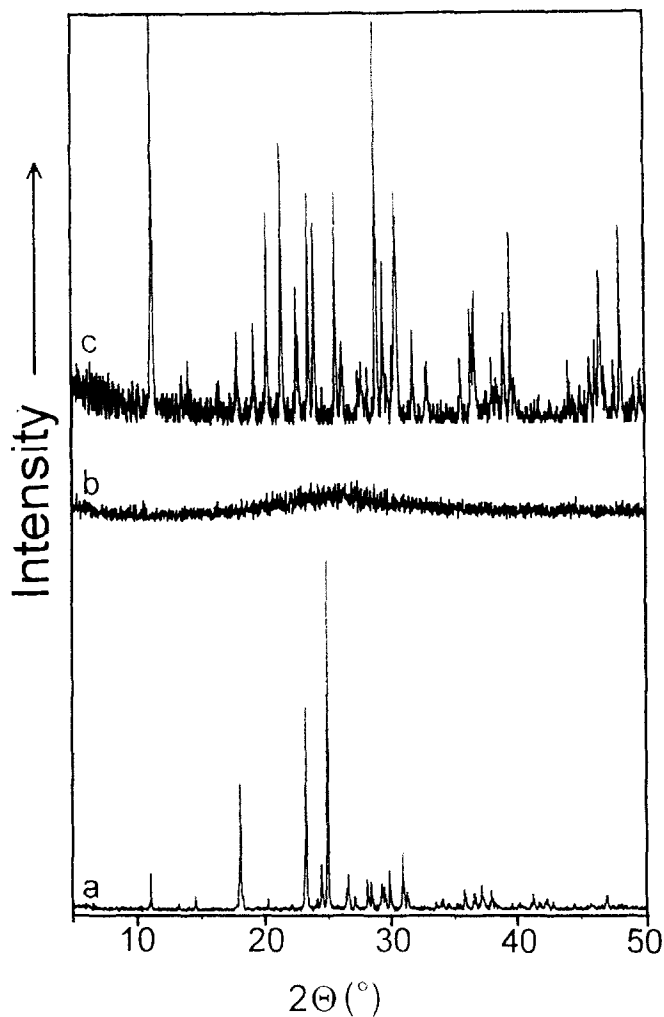


FIG. 3

X-ray powder diffractograms of the phosphates: (a) $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$, (b) amorphous phase, and (c) anhydrous compound.

The cyclohexaphosphate anions. The $\text{P}_6\text{O}_{18}^{6-}$ ring anion is centrosymmetrical, so it is located by only three crystallographically independent PO_4 tetrahedra, $\text{P}(1)\text{O}_4$, $\text{P}(2)\text{O}_4$, and $\text{P}(3)\text{O}_4$. The $\bar{1}$ internal symmetry is the most frequently observed symmetry; m , $m/3$, 3 , 3 and twofold local symmetry have also been seen in the $\text{P}_6\text{O}_{18}^{6-}$ anions characterized already. The values of the three P–P–P angles are different and are quite similar to those measured in a $\text{P}_6\text{O}_{18}^{6-}$ anion with the same internal symmetry. However, they are significantly different from what is observed in a $\text{P}_6\text{O}_{18}^{6-}$ anion with different internal symmetry where, for instance, the P–P–P angles are 108.51° in $(\text{NH}_4)_6\text{P}_6\text{O}_{18}\cdot \text{H}_2\text{O}$ (6) and 87.47° , 114.38° , and 115.57° in $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$ (7).

TABLE 3
Final Atomic Coordinates and B_{eq} for the Non-Hydrogen Atoms,
 B_{iso} for H Atoms, with Esd Given in Parentheses

Atoms	x(σ)	y(σ)	z(σ)	$B_{eq}(\sigma)$
Cs	0.07876 (4)	0.29194(3)	0.04709(4)	2.622(5)
Ca	0.59555 (7)	0.10208(6)	0.28211(8)	1.13(1)
P(1)	0.1005(1)	-0.01844(8)	0.8385(1)	1.12(1)
P(2)	0.6796(1)	0.11371(8)	0.8654(1)	1.04(1)
P(3)	0.7392(1)	0.51725(8)	0.1498(1)	1.11(1)
O(E11)	0.8911 (4)	0.8981(3)	0.1627(4)	2.50(7)
O(E12)	0.8191(3)	0.0831(3)	0.2349(3)	2.06(5)
O(L12)	0.8432(3)	0.0611(3)	0.9933(3)	2.03(5)
O(E21)	0.6867(4)	0.2677(2)	0.3914(3)	2.07(6)
O(E22)	0.4668(3)	0.5524(3)	0.6510(3)	2.22(6)
O(L23)	0.2859(3)	0.9061(2)	0.2781(3)	1.32(4)
O(E31)	0.2476(3)	0.9881(3)	0.4894(3)	1.85(5)
O(E32)	0.3825(3)	0.3998(3)	0.8566(3)	1.84(5)
O(L31)	0.9136(3)	0.5622(2)	0.2732(3)	1.44(5)
O(W)	0.5761(4)	0.7008(3)	0.4475(4)	2.71(7)
				B_{iso}
H(1W)	0.557(6)	0.737(6)	0.980(7)	4(2)
H(2W)	0.636(7)	0.849(6)	0.015(8)	5(2)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i b_j \beta_{ij}$$

The local geometry around the PO_4 tetrahedra (P–O and O–O distances, O–P–O and P–O–P angles) is similar to that commonly observed in cyclic or linear condensed phos-

TABLE 4
Anisotropic Thermal Parameters for $Ca_2Cs_2P_6O_{18} \cdot 2H_2O^*$

Name	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Cs	0.01110(3)	0.00399(2)	0.00816(3)	-0.00274(5)	0.00858(4)	0.00017(4)
Ca	0.00375(5)	0.00196(3)	0.00446(5)	-0.00032(8)	0.00487(7)	-0.00025(8)
P(1)	0.00375(7)	0.00235(5)	0.00327(7)	0.0005(1)	0.0035(1)	0.0007(1)
P(2)	0.00376(7)	0.00164(4)	0.00348(7)	0.0005(1)	0.0030(1)	-0.0003(1)
P(3)	0.00326(7)	0.00252(5)	0.00348(7)	-0.0007(1)	0.0038(1)	0.0000(1)
O(E11)	0.0099(4)	0.0024(2)	0.0099(4)	-0.0008(5)	0.0074(6)	0.0018(5)
O(E12)	0.0063(3)	0.0050(2)	0.0063(2)	-0.0007(4)	0.0089(3)	-0.0024(4)
O(L12)	0.0055(3)	0.0055(2)	0.0040(2)	0.0055(4)	0.0041(4)	0.0035(4)
O(E21)	0.0121(4)	0.0015(2)	0.0077(3)	-0.0010(4)	0.0103(5)	-0.0002(4)
O(E22)	0.0069(3)	0.0044(2)	0.0089(3)	0.0055(4)	0.0108(4)	0.0060(4)
O(L23)	0.0055(2)	0.0024(2)	0.0037(2)	0.0017(3)	0.0045(3)	0.0016(3)
O(E31)	0.0071(3)	0.0044(2)	0.0039(2)	0.0028(4)	0.0063(4)	0.0015(4)
O(E32)	0.0052(2)	0.0032(2)	0.0084(3)	0.0018(4)	0.0086(4)	0.0027(4)
O(L31)	0.0035(2)	0.0026(2)	0.0054(2)	-0.0010(3)	0.0033(4)	-0.0026(4)
O(W)	0.0127(5)	0.0037(2)	0.0062(3)	0.0015(6)	0.0045(6)	-0.0017(5)

*The formula used here is $\exp[-(b_{11} h^2 + b_{22} k^2 + b_{33} l^2 + b_{12} hk + b_{13} hl + b_{23} kl)]$.

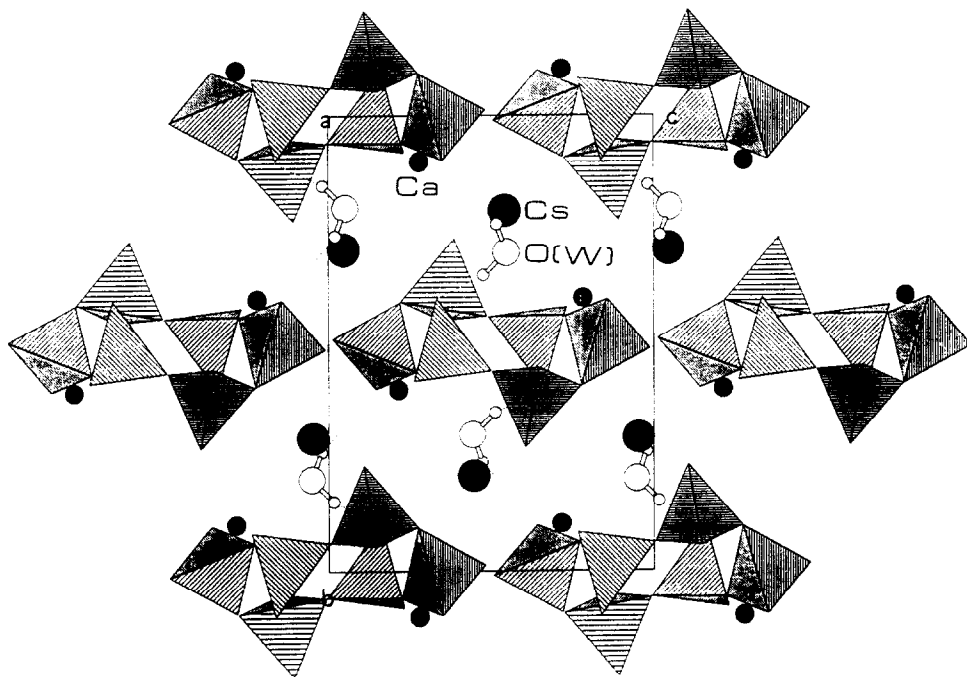


FIG. 4

A projection along the \vec{a} direction of $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot\text{H}_2\text{O}$. The phosphoric anion rings are given in tetrahedral representation.

phoric anions. The bridging P–O bonds in the tetrahedra are longer than the terminal bonds and the largest O–P–O angles in the tetrahedra correspond to the shortest P–O and the longest O–O distances (Table 4). This is probably explained by the effect of mutual repulsion of the nonbridging O atoms.

Cation environments. Within a coordination sphere of 2.5 Å, the Ca atom has sixfold coordination formed by one water molecule and five external oxygen atoms belonging to three P_6O_{18} rings. CaO_6 octahedra is slightly distorted because O–Ca–O angles (Table 4) range from 83.61 to 176.63 and Ca–O distances between 2.272 and 2.419 Å. The shortest distance Ca–Ca is 5.62 Å.

The cesium atom is coordinated, within a range of 3.5 Å, by eight oxygen neighbors including one water molecule and seven external oxygen atoms of the PO_4 tetrahedra. CsO_8 polyhedra formed from this environment are square antiprisms. Each one of the latter joins P_6O_{18} rings, while each anionic ring connects six Cs polyhedra and eight Ca octahedra. The shortest distance Cs–Cs is 5.05 Å. All of the PO_4 tetrahedra are monodentate with respect to calcium and cesium atoms.

The water molecules involved in the coordination polyhedra of Ca and Cs atoms are located between the layers. Figure 4 shows their role, through the hydrogen bonds, in the cohesion of the adjacent layers. Bond distances and angles of the H-bond network are given in Table 4.

TABLE 5
Main Interatomic Distances (Å) and Bond Angles (°) in $\text{Ca}_2\text{Cs}_2\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$
with Esd Given in Parentheses

P(1)O₄ Tetrahedron				
P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	<u>1.477 (4)</u>	2.551 (5)	2.512 (5)	2.564 (4)
O(E12)	119.5 (2)	<u>1.476 (4)</u>	2.515 (5)	2.480 (4)
O(L12)	109.9 (2)	110.1 (2)	<u>1.589 (3)</u>	2.364 (3)
O(L13)	112 (2)	112.2 (2)	95.3 (2)	<u>1.611 (3)</u>
P(2)O₄ Tetrahedron				
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	<u>1.471 (3)</u>	2.542 (4)	2.479 (4)	2.473 (5)
O(E22)	119.5 (2)	<u>1.472 (3)</u>	2.516 (3)	2.534 (5)
O(L12)	108.2 (2)	110.5 (2)	<u>1.589 (3)</u>	2.427 (4)
O(L23)	107 (2)	110.8 (2)	98.9 (2)	<u>1.604 (3)</u>
P(3)O₄ Tetrahedron				
P(3)	O(E31)	O(E32)	O(L23)	O(L13)
O(E31)	<u>1.480 (3)</u>	2.568 (5)	2.484 (4)	2.504 (4)
O(E32)	120.1 (2)	<u>1.484 (3)</u>	2.534 (4)	2.442 (3)
O(L23)	107.4 (2)	110.3 (2)	<u>1.601 (3)</u>	2.524 (4)
O(L13)	109 (2)	104.7 (2)	104.2 (1)	<u>1.597 (2)</u>
P(1) – P(2)	2.937(1)		P(1) – O(L12) – P(2)	135.1(2)
P(1) – P(3)	2.950(1)		P(1) – O(L13) – P(3)	133.7(2)
P(2) – P(3)	2.909(1)		P(2) – O(L23) – P(3)	130.3(2)
		P(2) – P(1) – P(3)	133.8(5)	
		P(1) – P(2) – P(3)	104.1(4)	
		P(1) – P(3) – P(2)	93.6(3)	
CaO₆ Octahedron				
Ca – O(E12)	2.292(3)		Ca – O(E31)	2.331(3)
Ca – O(E21)	2.272(3)		Ca – O(E32)	2.361(3)
Ca – O(E22)	2.290(3)		Ca – O(W)	2.419(3)
CsO₈ Polyhedron				
Cs – O(E11)	3.212(4)		Cs – O(E21)	3.257(3)
Cs – O(E11)	3.048(4)		Cs – O(E31)	3.275(3)
Cs – O(E12)	3.289(3)		Cs – O(L31)	3.310(3)
Cs – O(L12)	3.441(3)		Cs – O(W)	3.309(4)
Hydrogen Bond				
O(W)–H···O	O(W)–H	H···O	O(W)–H···O	O(W)–O
O(W)–H(1W)···O(E32)	0.86 (8)	2.23 (7)	154 (4)	3.02 (5)
O(W)–H(2W)···O(E11)	0.89 (6)	2.19 (5)	143 (6)	2.94 (4)
		H(1W) – O(W) – H(2W)	118 (6)	

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