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# Crystal structure and proton conductivity of a new $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ phase in the caesium diand monohydrogen orthophosphate system

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The  $M_xH_y(AO_4)_z$  acid salts ( $M = Cs, Rb, K, Na, Li, NH_4; A = S, Se, As, P$ ) exhibit ferroelectric properties. The solid acids have low conductivity values and are of interest with regard to their thermal properties and proton conductivity. The crystal structure of caesium dihydrogen orthophosphate monohydrogen orthophosphate dihydrate, Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, has been solved. The compound crystallizes in the space group Pbca and forms a structure with strong hydrogen bonds connecting phosphate tetrahedra that agrees well with the IR spectra. The dehydration of Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O with the loss of two water molecules occurs at 348–433 K. Anhydrous  $Cs_3(H_{1.5}PO_4)_2$  is stable up to 548 K and is then converted completely into caesium pyrophosphate  $(Cs_4P_2O_7)$  and CsPO<sub>3</sub>. Anhydrous Cs<sub>3</sub>( $H_{1.5}PO_4$ )<sub>2</sub> crystallizes in the monoclinic C2 space group, with the unit-cell parameters a = 11.1693 (4), b = 6.4682 (2), c = 7.7442 (3) Å and  $\beta = 71.822 \ (2)^{\circ}$ . The conductivities of both compounds have been measured. In contrast to crystal hydrate  $Cs_3(H_1 _5PO_4)_2 \cdot 2H_2O$ , the dehydrated form has rather low conductivity values of  $\sim 6 \times 10^{-6}$ -10<sup>-8</sup> S cm<sup>-1</sup> at 373-493 K, with an activation energy of 0.91 eV.

### 1. Introduction

The family of acid salts with the general structural formula  $M_r H_v (AO_4)_r$  (M = Cs, Rb, K, Na, Li, NH<sub>4</sub>; A = S, Se, As, P) has been studied intensively due to their ferroelectric properties, which are promising for optical devices (Busch & Scherrer, 1935; Frazer & Pepinsky, 1953; Reese & May, 1967; Busch, 1987). The solid acids have low conductivity values ( $\sim 10^{-6}$ –  $10^{-9}$  S cm<sup>-1</sup> at room temperature) which are associated with proton hopping in the crystal structures with ordered hydrogen bonds related to the presence of local defects. Superionic phase transitions with a significant entropy change were detected in these systems in the 1980s and 1990s. Hightemperature superionic phases are characterized by structural disordering of the hydrogen-bond network, resulting in high mobility of the protons and an increase in the proton conductivity up to  $\sigma \sim 10^{-3}$ – $10^{-2}$  S cm<sup>-1</sup> at 373–523 K (Baranov et al., 1982, 1988; Preisinger et al., 1994).

Caesium dihydrogen phosphate in its superionic phase has one of the highest conductivity values among the numerous salts of the family (Preisinger *et al.*, 1994). A phase transition from the monoclinic ( $P2_1/m$ ) to the superionic cubic ( $Pm\overline{3}m$ ) phase of CsH<sub>2</sub>PO<sub>4</sub> is observed at 502 K. In the superionic phase, all H<sup>+</sup> ions participate in proton transfer, accounting for the high conductivity value,  $\sigma_{503 \text{ K}} = 6 \times 10^{-2} \text{ S cm}^{-1}$  (Preisinger *et al.*, 1994). Due to the high proton conductivity,

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CsH<sub>2</sub>PO<sub>4</sub> is promising as a material for proton membranes in electrochemical devices, in particular, in intermediatetemperature fuel cells (ITFCs). High electrochemical characteristics have been achieved for ITFCs with the CsH<sub>2</sub>PO<sub>4</sub> membrane (Boysen et al., 2004; Uda & Haile, 2005). For the disubstituted phosphate analogue, i.e. Cs<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O, the crystal structure, thermal properties and conductivity have been reported recently (Stöger & Weil, 2014; Lavrova et al., 2016; Ponomareva et al., 2017). Cs<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O crystallizes in the monoclinic space group  $P2_1/c$ , with lattice parameters a =7.4761 Å, b = 14.2125 Å, c = 7.9603 Å,  $\beta = 116.914^{\circ}$ , V =754.20 Å<sup>3</sup> and Z = 4. The distorted tetrahedra of the HPO<sub>4</sub><sup>2-</sup> anions are linked by short hydrogen bonds ( $O \cdot \cdot \cdot O = 2.579 \text{ Å}$ ), forming a chain along the c axis. Two symmetry-independent water molecules connect the chains into a three-dimensional hydrogen-bonding network ( $O \cdot \cdot \cdot O = 2.740 - 2.753$  Å). Cs<sub>2</sub>-HPO<sub>4</sub>·2H<sub>2</sub>O dehydrates in two stages with losses of 0.5 and 1.5 water molecules per asymmetric unit at temperatures of 333-373 and 373-433 K, respectively. Anhydrous Cs<sub>2</sub>HPO<sub>4</sub> is stable up to 673 K; at 603 K, it is completely converted to caesium pyrophosphate, Cs<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (Lavrova et al., 2016).

The conductivity measurements for  $Cs_2HPO_4 \cdot 2H_2O$  agree with the thermogravimetry and IR spectroscopy data (Ponomareva *et al.*, 2017). The proton conductivity of  $Cs_2HPO_4$ (~6 × 10<sup>-6</sup>-10<sup>-9</sup> S cm<sup>-1</sup> at 363–523 K) is comparable with the values for the low-temperature phase of  $CsH_2PO_4$ . Investigation of the  $(1 - x)CsH_2PO_4 - xCs_2HPO_4 \cdot yH_2O$  system in a wide range of compositions allowed us to find  $Cs_3$ -(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·yH<sub>2</sub>O, a previously unreported phase at x = 0.5. The existence of this phase affects markedly the transport and thermodynamic properties of the composite proton electrolytes based on these salts.



Figure 1

Electron microscopy photograph (top) and EDS spectrum (bottom) of the  $Cs_3(H_{1.5}PO_4)_2{\cdot}2H_2O$  single crystal.

Table 1	
Experimental details.	
Crystal data	
Chemical formula	$Cs_3(H_2PO_4)(HPO_4)\cdot 2H_2O$
$M_{ m r}$	627.73
Crystal system, space group	Orthorhombic, Pbca
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.4721 (5), 11.4369 (8), 14.8509 (11)
$V(Å^3)$	1269.12 (15)
Z	4
Radiation type	Μο Κα
$\mu \text{ (mm}^{-1})$	8.85
Crystal size (mm)	$0.20\times0.05\times0.02$
Data collection	
Diffractometer	Agilent Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2016)
$T_{\min}, T_{\max}$	0.453, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	17880, 1298, 1176
R <sub>int</sub>	0.086
$(\sin \theta / \lambda)_{\rm max} ({\rm \AA}^{-1})$	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.074, 1.05
No. of reflections	1298
No. of parameters	79
No. of restraints	1
H-atom treatment	Only H-atom coordinates refined
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} (e {\rm \AA}^{-3})$	0.85, -1.14

Computer programs: CrysAlis PRO (Rigaku OD, 2016), SHELXS97 (Sheldrick, 2008), SHELXL2016 (Sheldrick, 2015), shelXle (Hübschle et al., 2011) and DIAMOND (Brandenburg & Putz, 1999).

The present work aims to study the crystal structure of the new  $Cs_3(H_{1.5}PO_4)_2 \cdot yH_2O$  compound in relation to its thermal properties and proton conductivity.

### 2. Experimental

### 2.1. Synthesis and crystallization

Single crystals of the starting  $Cs_2HPO_4 \cdot 2H_2O$  and  $CsH_2PO_4$ compounds were grown by isothermal evaporation at 308 K and at room temperature from aqueous solutions of  $Cs_2CO_3$ (special purity grade) and  $H_3PO_4$  (special purity grade) taken in molar ratios of 1:1 and 1:2, respectively. Single crystals of  $Cs_3(H_{1.5}PO_4)_2 \cdot yH_2O$  were grown in a similar way, *i.e.* by the isothermal evaporation of aqueous solutions of  $Cs_2HPO_4$ .- $2H_2O$  and  $CsH_2PO_4$  taken in an equimolar ratio at 308 K.

#### 2.2. PXRD and EDS analysis

The phase composition of the parent salts was investigated by powder X-ray diffraction (PXRD). PXRD patterns were collected on a Bruker D8 Advance diffractometer with Cu  $K\alpha$ radiation (one-dimensional Lynx-Eye detector and  $K\beta$  filter). The PXRD patterns of the initially synthesized salts are completely in agreement with previous results (Stöger & Weil, 2014; Lavrova *et al.*, 2016; Ueso & Kobayashi, 1976; Matsunaga *et al.*, 1980; Preisinger *et al.*, 1994). The ratio of caesium to phosphorus in the crystals was estimated by energydispersive X-ray spectroscopy (EDS) using a Thermo Scientific EDS Spectrometer with a Silicon Drift UltraDry 30 detector on a Hitachi 3400N scanning electron microscope. The EDS spectra were processed using the Thermo Scientific NSS software package. An analysis of the spectrum showed the content of Cs atoms in the synthesized compound to be 1.5 times higher than the content of P atoms (Fig. 1), corresponding to the  $Cs_3(H_1 _5PO_4)_2 \cdot 2H_2O$  formula. The content of crystal water in a single crystal was estimated from the thermogravimetric data. IR absorption spectra of the powders were registered using a Digilab Excalibur 3100 spectrometer with a ZnSe crystal in the frequency range  $4000-600 \text{ cm}^{-1}$ . Differential scanning calorimetry (DSC) and thermogravimetry (TGA) data were obtained using a NETZSCH STA 449 F/1/1 JUPITER thermoanalytical complex in the temperature range 293–713 K at a heating rate of 2 K min<sup>-1</sup> under argon with a flow rate of 30 ml min<sup>-1</sup>.

#### 2.3. Refinement

The crystal structure of Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O has been determined from single-crystal X-ray diffraction (SC-XRD). All heavy atoms were refined anisotropically without restraints. H-atom coordinates were refined, with  $U_{iso}(H) =$  $1.2U_{eq}(O)$ . The H2 atom is involved in a strong  $O-H \cdots O$ hydrogen bond and was refined freely; its central position suggested the symmetric nature of the hydrogen bond. We selected this model with the H atom lying at a symmetry centre instead of that with the H atom statistically disordered between general positions since it gives 0.5-1% lower R factor values and the only peak in the difference electron-density map is midway between the donor and acceptor O2 atoms. A distance restraint of 0.82 (2) Å was used for the O3-H3 bond in a phosphate anion. Data collection and refinement parameters, as well as crystal data, for Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O are summarized in Table 1. Indexing and refinement of the lattice



Figure 2

PXRD pattern of  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ . The black solid line with circles is the observed pattern, the red solid line is the calculated pattern and the vertical markers are the positions of the Bragg reflections for  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ . parameters for  $Cs_3(H_{1.5}PO_4)_2$  were carried out from the PXRD pattern created by the *TOPAS* software (Coelho *et al.*, 2011).

### 2.4. Conductivity measurements

For conductivity measurements, the samples were pressed with silver electrodes into pellets (diameter 7 mm, thickness ~2.3 mm), with a relative density of 96–98%. The conductivity was measured in the frequency range 1–3.3 MHz by a twoelectrode circuit alternating current impedance meter IPU-1RLC-1/2008, an instrument for the precise measurements of electrochemical characteristics developed by the Institute of Control Sciences of the Russian Academy of Sciences. The higher frequency minimum/intercept along the x axis (real Z) of the impedance plots was used to calculate the bulk resis-



Figure 3 (a) The *cb* and (b) the *ab* projection of the  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$  crystal structure.

tance of the samples. The measurements were carried out on heating and on cooling, with a rate of  $\sim 0.5-1.0 \text{ K min}^{-1}$ , as well as during long-term storage at 513 K for at least 1–2 h in air with  $\sim 10-15\%$  relative humidity (RH). In the latter case, the steady-state values of the conductivity were reached.

### 3. Results and discussion

Fig. 2 presents the PXRD pattern of the synthesized Cs<sub>3</sub>- $(H_{1.5}PO_{4})_{2}$ ·2H<sub>2</sub>O compound. A single-crystal diffraction analysis showed that this compound crystallizes in the orthorhombic space group *Pbca*. A fragment of the crystal structure is shown schematically in Fig. 3. The asymmetric unit contains two Cs atoms. Cs1 is twleve-coordinated to O atoms, with Cs-O distances ranging from 3.146 (4) to 3.712 (5) Å, and the coordination sphere of Cs2 is defined by eight O atoms, with Cs–O distances ranging from 3.130(5) to 3.479(4) Å. The coordination environments of the Cs1 and Cs2 atoms are located at mean distances of 3.380 and 3.258 Å, respectively, which agree with the mean radius of 1.88 Å for twelvecoordinated and 1.74 Å for eight-coordinated Cs<sup>+</sup> ions (Shannon, 1976), assuming an oxygen-anion radius of 1.40 Å. The two symmetry-independent Cs<sup>+</sup> cations are located in the layers parallel to (001) or in the voids in the [PO<sub>3</sub>(OH)]<sup>-</sup> layers.

Unlike in the known mixed divalent cation phosphates  $MBa_2(HPO_4)_2(H_2PO_4)_2$  (M = Ca, Cd, Mn) (Ben Tahar *et al.*, 1999; Taher *et al.*, 2001; Sun *et al.*, 2012), only one type of phosphate tetrahedron was observed in  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ .



Figure 4

Schematic representation of the network of hydrogen bonds in an *ac* projection of the  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$  structure. Hydrogen bonds are shown as dashed lines.

The hydrogen phosphate species have typical tetrahedral geometry, with an average P–O distance of 1.534 Å, which agrees with the length expected for a P–O bond. All four O atoms participate in hydrogen-bond formation. The P–O1 distance is 1.513 (4) Å and atom O1 forms two medium-strength hydrogen bonds with two hydrate water molecules. The P–O2 distance corresponds to the oxygen apex of the [PO<sub>4</sub>] tetrahedron that is involved in the strong symmetric hydrogen bond, *i.e.* O2–H2···O2<sup>i</sup> (see Table 2 for hydrogen-bond details and symmetry codes). The shortest [P–O4 = 1.498 (4) Å] and longest [P–O3 = 1.590 (4) Å] distances



#### Figure 5

The IR spectra of  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ , **1**, and  $Cs_2HPO_4 \cdot 2H_2O$ , **2**, showing (*a*) the region of hydrogen bonds and (*b*) the region of phosphate tetrahedra.

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Table 2Hydrogen-bond geometry (Å, °).

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdots A$
$\begin{array}{c} O2 - H2 \cdots O2^{i} \\ O3 - H3 \cdots O4^{ii} \\ O5 - H5A \cdots O1^{iii} \\ O5 - H5B \cdots O1^{iv} \end{array}$	1.22 (1)	1.22 (1)	2.445 (7)	180 (1)
	0.80 (2)	1.75 (2)	2.549 (5)	177 (6)
	0.82 (8)	1.90 (8)	2.713 (6)	175 (7)
	0.90 (8)	1.82 (8)	2.725 (6)	176 (7)

Symmetry codes: (i) -x + 2, -y, -z; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z$ ; (iii) x - 1, y, z; (iv)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ .

correspond to the formation of an O3-H3...O4<sup>ii</sup> hydrogen bond. The symmetry of the [PO<sub>4</sub>] groups is close to tetrahedral, as is evidenced by small (less than  $5^{\circ}$ ) deviations of the O-P-O angles from the value of 109.28° for an ideal tetrahedron. The crystal structure is formed by tetrahedra connected via strong O2-H2···O2<sup>i</sup> and O3-H3···O4<sup>ii</sup> hydrogen bonds, forming undulating sheets parallel to (001) (Fig. 3). Adjacent sheets are bound to each other via mediumstrength hydrogen bonds involving two symmetricallyequivalent water molecules, forming a three-dimensional network. The overall hydrogen-bonding scheme in Cs3- $(H_{1.5}PO_4)_2 \cdot 2H_2O$  is illustrated in Fig. 4. The IR spectra (Fig. 5) agree with the existence of a network of strong hydrogen bonds. The broad band at  $\sim$ 3145 cm<sup>-1</sup> is associated with the stretching vibrations of the crystal water molecules involved in the hydrogen-bond network. The ABC-type broad bands of high-frequency H-atom vibrations have been interpreted as O-H stretching modes in Fermi resonance with a combination involving mainly the O-H bending vibrations (Hadzi &



Figure 6 DSC and TGA curves for the powders of  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ , **1**, and  $Cs_5HPO_4 \cdot 2H_2O$ , **2**.

Bratos, 1976). Three bands (~2790, 2350 and 1745 cm<sup>-1</sup>) are observed in the O–H stretching and bending region of the IR spectrum, confirming the presence of strong hydrogen bonds. These spectral characteristics have been observed in a variety of strong hydrogen-bonded solids having O···O distances varying from 2.4 to 2.6 Å (Taher *et al.*, 2001; Sun *et al.*, 2012; Marchon & Novak, 1983; Baran *et al.*, 1989). The band with a maximum lying at 2350 cm<sup>-1</sup> and a shoulder around 2200 cm<sup>-1</sup> may be related to the presence of two different types of hydrogen bonds with different lengths. The broad band at ~750 cm<sup>-1</sup> is characterized by out-of-plane-bending vibrations, in accordance with the literature (Marchon & Novak, 1983; Baran *et al.*, 1989).

The differential scanning calorimetry (DSC) and thermogravimetry (TGA) data are shown in Fig. 6. TGA and DSC curves for Cs<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O are also shown for comparison. According to the TGA,  $Cs_3(H_1 \ _5PO_4)_2 \cdot 2H_2O$  is stable up to 343 K; only a slight weight loss (less than  $\sim 0.15\%$ ) occurs until 343 K, which is related to the removal of adsorbed water from the surface of the hygroscopic compound when stored in air. Three endothermic effects are observed on dehydration of Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O and its further thermal decomposition. The first effect, with an onset temperature of  $\sim$ 318 K, is associated with the removal of crystalline water and agrees with the theoretical weight loss of 5.73%. Anhydrous  $Cs_3(H_{1.5}PO_4)_2$  is stable up to 548 K. Its thermal decomposition, with the formation Cs<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and CsPO<sub>3</sub>, occurs in two stages. The first stage is observed at 548-598 K and the second in the temperature range 613-673 K, with a total weight loss of 4.56%. The observed total weight loss of the sample heated to 703 K is 10.2%, which agrees well with the theoretical value for  $Cs_3(H_1 _5PO_4)_2 \cdot 2H_2O$  (10.29%). Comparing the DSC and TGA data for the two crystal hydrates, *i.e.*  $Cs_3(H_{1.5}PO_4)_2$ .  $2H_2O$  and  $Cs_2HPO_4 \cdot 2H_2O$ , one can see that the dehydration proceeds in one and two stages, respectively, in accordance with the nonequivalence of Cs2HPO4·2H2O crystal water molecules. The region of thermal stability of the dehydrated



PXRD pattern of  $Cs_3(H_{1.5}PO_4)_2$  at 433 K. Vertical lines represent the positions of the Bragg reflections in a monoclinic C2 cell.

compounds differs markedly and is 383 K narrower for the  $Cs_3(H_{1.5}PO_4)_2$  salt.

The space group and unit-cell parameters of anhydrous  $Cs_3(H_{1.5}PO_4)_2$  at 433 K were also defined. *TOPAS* (Coelho *et al.*, 2011) was used to index the diffraction pattern and refine the unit-cell parameters. The PXRD pattern of  $Cs_3(H_{1.5}PO_4)_2$  (Fig. 7) was indexed as a monoclinic *C*2 cell, with unit-cell parameters *a* = 11.1693 (4) Å, *b* = 6.4682 (2) Å, *c* = 7.7442 (3) Å and  $\beta$  = 71.822 (2)°.

The temperature dependence of the proton conductivity agrees with the structural and thermodynamic characteristics (Fig. 8). The dehydration of  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$  starts above 348 K and is accompanied by crystal fragmentation; therefore, the conductivity was measured for polycrystalline samples. The conductivity of the initial  $Cs_3(H_{1.5}PO_4)_2$ ·2H<sub>2</sub>O at room temperature is  $\sim 6 \times 10^{-5}$  S cm<sup>-1</sup> (RH  $\sim 10\%$ ). This rather high conductivity value is related to the presence of crystal water molecules in the structure. The proton conductivity values at low temperatures depended significantly on the RH. This is common for crystal hydrates (Colomban, 1992; Kreuer, 1997b). At T > 348 K, the conductivity increased sharply, reaching  $\sim 8 \times 10^{-3}$ - $10^{-2}$  S cm<sup>-1</sup>. This increase is related to the dehydration of the weakly bound water molecules, which are trapped in the bulk of the sample down to  $\sim$ 453 K, providing conductive channels and accounting for the high proton conductivity. The removal of the crystal water from the dense  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$  samples is slow, and this leads to values of the conductivity as high as  $10^{-2}$  S cm<sup>-1</sup> when heating the samples at 373–453 K. A further increase in temperature and long-term storage at 493 K results in a conductivity decrease of more than three orders of magnitude, as the dehydration is completed. The conductivity of anhydrous  $Cs_3(H_{1,5}PO_4)_2$  is characterized by linear Arrhenius dependence, with the low and reproducible values in subsequent heating-cooling cycles at 373–493 K (Fig. 8) being  $\sim 6 \times 10^{-6}$ –  $10^{-8}$  S cm<sup>-1</sup> and the activation energy of conductivity being



The temperature dependencies of conductivity for  $Cs_3(H_{1.5}PO_4)_2 \cdot yH_2O$  (heating mode) and  $Cs_3(H_{1.5}PO_4)_2$  (cooling mode).

~0.91 eV. The processes defining the temperature dependence of conductivity are consistent with the DSC and TGA data. The proton conductivity of  $Cs_3(H_{1.5}PO_4)_2$  is comparable with that of the low-temperature  $(P2_1/m)$  phase of  $CsH_2PO_4$ (Baranov *et al.*, 1988; Preisinger *et al.*, 1994; Ueso & Kobayashi, 1976; Matsunaga *et al.*, 1980) and of  $Cs_2HPO_4$ (putative structure in the C2/c group) (Stöger & Weil, 2014; Ponomareva *et al.*, 2017). In these phases, the activation energy of conductivity is determined by the energy of the formation of proton defects and by their mobility according to the de Grotthuss mechanism (de Grotthuss, 1806; Kreuer, 1997*a*). A similar mechanism of proton transfer is likely for  $Cs_3(H_{1.5}PO_4)_2$ .

### 4. Conclusion

A new compound,  $Cs_3(H_{1.5}PO_4)_2 \cdot 2H_2O$ , has been synthesized and its crystal structure has been determined for the first time. Cs<sub>3</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O crystallizes in the *Pbca* space group and is characterized by a three-dimensional hydrogen-bond network that consists of undulating sheets of tetrahedra connected via medium-strength hydrogen bonds involving two symmetrically equivalent water molecules. Phosphate tetrahedra in the sheets were shown to be bonded by strong hydrogen bonds with lengths of 2.445 (7) and 2.549 (5) Å. Two symmetrically independent twelve- and eight-coordinated Cs<sup>+</sup> cations are located in layers parallel to (001) or in the voids in  $[PO_3(OH)]^-$  layers. The hydrogen bonds in the crystal structure are strong and ordered, which was confirmed by IR spectroscopic analysis. The anhydrous  $Cs_3(H_1 \ _5PO_4)_2$  phase was determined to belong to the monoclinic C2 space group. The proton conductivities of the new compound, Cs<sub>3</sub>- $(H_{1.5}PO_4)_2 \cdot 2H_2O$ , and of its dehydrated form are related to their crystal structures. The proton conductivity of Cs3- $(H_{1.5}PO_4)_2 \cdot 2H_2O$  is  $10^{-5}$  S cm<sup>-1</sup> at T = 303 K. On heating, as dehydration starts, the proton conductivity first increases sharply, reaching a value of  $\sim 8 \times 10^{-3}$ - $10^{-2}$  S cm<sup>-1</sup>, as water is trapped in the sample, but then decreases to  $6 \times 10^{-6}$ – $10^{-8}$  S  $cm^{-1}$  at 373–493 K; dehydration to the anhydrous  $Cs_3(H_{1.5}PO_4)_2$  phase is complete at T > 433 K.

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### Acta Cryst. (2017). C73 [https://doi.org/10.1107/S2053229617012335]

Crystal structure and proton conductivity of a new Cs<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)(HPO<sub>4</sub>)·2H<sub>2</sub>O phase in the caesium di- and monohydrogen orthophosphate system

## Valentina Ponomareva, Irina Bagryantseva, Boris Zakharov, Natalia Bulina, Galina Lavrova and Elena Boldyreva

### **Computing details**

Data collection: *CrysAlis PRO* (Rigaku OD, 2016); cell refinement: *CrysAlis PRO* (Rigaku OD, 2016); data reduction: *CrysAlis PRO* (Rigaku OD, 2016); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015) and ShelXle (Hübschle *et al.*, 2011); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015).

**(I**)

### Crystal data

Cs<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)(HPO<sub>4</sub>)·2H<sub>2</sub>O  $M_r = 627.73$ Orthorhombic, *Pbca*  a = 7.4721 (5) Å b = 11.4369 (8) Å c = 14.8509 (11) Å V = 1269.12 (15) Å<sup>3</sup> Z = 4F(000) = 1128

### Data collection

Agilent Xcalibur Ruby Gemini ultra diffractometer Radiation source: sealed X-ray tube Detector resolution: 10.3457 pixels mm<sup>-1</sup>  $\omega$  scan Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2016)  $T_{\min} = 0.453, T_{\max} = 1.000$ 

### Refinement

Refinement on  $F^2$ Least-squares matrix: full  $R[F^2 > 2\sigma(F^2)] = 0.030$  $wR(F^2) = 0.074$ S = 1.051298 reflections 79 parameters 1 restraint  $D_{\rm x} = 3.285 \text{ Mg m}^{-3}$ Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ Å}$ Cell parameters from 9404 reflections  $\theta = 2.7-29.2^{\circ}$  $\mu = 8.85 \text{ mm}^{-1}$ T = 296 KBlock, colourless  $0.20 \times 0.05 \times 0.02 \text{ mm}$ 

17880 measured reflections 1298 independent reflections 1176 reflections with  $I > 2\sigma(I)$   $R_{int} = 0.086$   $\theta_{max} = 26.4^{\circ}, \ \theta_{min} = 3.5^{\circ}$   $h = -9 \rightarrow 9$   $k = -14 \rightarrow 14$  $l = -18 \rightarrow 18$ 

Primary atom site location: structure-invariant direct methods Secondary atom site location: difference Fourier map Hydrogen site location: difference Fourier map Only H-atom coordinates refined  $w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 3.3232P]$ where  $P = (F_o^2 + 2F_c^2)/3$   $(\Delta/\sigma)_{\rm max} = 0.001$  $\Delta \rho_{\rm max} = 0.85 \text{ e } \text{\AA}^{-3}$ 

### $\Delta \rho_{\rm min} = -1.14 \text{ e} \text{ Å}^{-3}$

### Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters  $(Å^2)$ 

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
Cs1	0.07728 (4)	0.82817 (3)	0.17311 (2)	0.02937 (14)	
Cs2	0.000000	0.500000	0.000000	0.03806 (17)	
P1	0.99034 (15)	0.17285 (10)	0.09057 (8)	0.0220 (3)	
01	1.0725 (5)	0.1525 (4)	0.1823 (3)	0.0364 (10)	
O2	0.9101 (5)	0.0612 (3)	0.0501 (3)	0.0389 (9)	
H2	1.000000	0.000000	0.000000	0.047*	
O3	0.8240 (5)	0.2562 (3)	0.1086 (2)	0.0337 (8)	
Н3	0.759 (7)	0.262 (5)	0.066 (3)	0.040*	
04	1.1154 (5)	0.2333 (4)	0.0270 (3)	0.0426 (9)	
05	0.3745 (7)	0.0228 (4)	0.2003 (3)	0.0423 (10)	
H5A	0.282 (10)	0.061 (6)	0.198 (5)	0.051*	
H5B	0.445 (9)	0.066 (6)	0.237 (5)	0.051*	

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0299 (2)	0.0290 (2)	0.0292 (2)	-0.00062 (11)	0.00038 (12)	0.00102 (11)
Cs2	0.0458 (3)	0.0320 (3)	0.0363 (3)	0.00700 (19)	-0.0036 (2)	0.00316 (18)
P1	0.0209 (6)	0.0258 (6)	0.0194 (6)	-0.0006 (4)	0.0015 (4)	-0.0018 (5)
O1	0.028 (2)	0.051 (2)	0.030(2)	0.0072 (16)	-0.0026 (14)	0.0015 (17)
O2	0.037 (2)	0.0306 (19)	0.049 (2)	-0.0061 (15)	0.0049 (17)	-0.0183 (17)
O3	0.0289 (19)	0.042 (2)	0.030(2)	0.0121 (15)	-0.0054 (15)	-0.0126 (16)
O4	0.049 (2)	0.046 (2)	0.033 (2)	-0.0098 (19)	0.0127 (18)	-0.0004 (18)
05	0.046 (2)	0.032 (2)	0.049 (3)	0.0103 (19)	-0.017 (2)	-0.0093 (19)

Geometric parameters (Å, °)

Cs1—O1 <sup>i</sup>	3.146 (4)	Cs2—O5 <sup>viii</sup>	3.130 (5)
Cs1—O5 <sup>ii</sup>	3.170 (5)	Cs2—O4 <sup>vi</sup>	3.194 (4)
Cs1—O3 <sup>iii</sup>	3.253 (4)	Cs2—O4 <sup>ix</sup>	3.194 (4)
Cs1—O5 <sup>iv</sup>	3.284 (4)	Cs2—O2 <sup>iii</sup>	3.230 (4)
Cs1—O1 <sup>v</sup>	3.302 (4)	Cs2—O2 <sup>viii</sup>	3.230 (4)
Cs1—O4 <sup>v</sup>	3.341 (4)	Cs2—O3 <sup>vi</sup>	3.479 (4)
Cs1—O4 <sup>vi</sup>	3.376 (4)	Cs2—O3 <sup>ix</sup>	3.479 (4)
Cs1—O3 <sup>i</sup>	3.424 (4)	Cs2—P1 <sup>vi</sup>	3.9767 (12)
Cs1—O2 <sup>vii</sup>	3.465 (4)	Cs2—P1 <sup>ix</sup>	3.9767 (12)
Cs1—O5 <sup>iii</sup>	3.534 (4)	P1—O4	1.498 (4)

Cs1—O2 <sup>vi</sup>	3.549 (4)	P1—O1	1.513 (4)
Cs1—O1 <sup>vii</sup>	3.712 (5)	P1—O2	1.533 (4)
Cs2—O5 <sup>iii</sup>	3.130 (5)	Р1—О3	1.590 (4)
O1 <sup>i</sup> —Cs1—O5 <sup>ii</sup>	127.65 (11)	$O2^{viii}$ — $Cs2$ — $P1^{vi}$	96.25 (7)
O1 <sup>i</sup> —Cs1—O3 <sup>iii</sup>	73.22 (10)	$O3^{vi}$ — $Cs2$ — $P1^{vi}$	23.42 (6)
O5 <sup>ii</sup> —Cs1—O3 <sup>iii</sup>	149.39 (10)	$O3^{ix}$ — $Cs2$ — $P1^{vi}$	156.58 (6)
$O1^{i}$ —Cs1—O5 <sup>iv</sup>	83.00 (11)	O5 <sup>iii</sup> —Cs2—P1 <sup>ix</sup>	76.26 (8)
O5 <sup>ii</sup> —Cs1—O5 <sup>iv</sup>	76.96 (9)	O5 <sup>viii</sup> —Cs2—P1 <sup>ix</sup>	103.74 (8)
O3 <sup>iii</sup> —Cs1—O5 <sup>iv</sup>	85.11 (11)	O4 <sup>vi</sup> —Cs2—P1 <sup>ix</sup>	159.35 (7)
$O1^{i}$ —Cs1—O1 <sup>v</sup>	82.24 (11)	O4 <sup>ix</sup> —Cs2—P1 <sup>ix</sup>	20.65 (7)
O5 <sup>ii</sup> —Cs1—O1 <sup>v</sup>	82.35 (10)	O2 <sup>iii</sup> —Cs2—P1 <sup>ix</sup>	96.25 (7)
$O3^{iii}$ — $Cs1$ — $O1^{v}$	126.06 (10)	O2 <sup>viii</sup> —Cs2—P1 <sup>ix</sup>	83.75 (7)
$O5^{iv}$ —Cs1—O1 <sup>v</sup>	138.97 (11)	O3 <sup>vi</sup> —Cs2—P1 <sup>ix</sup>	156.58 (6)
$O1^{i}$ —Cs1—O4 <sup>v</sup>	118.72 (10)	$O3^{ix}$ —Cs2—P1 <sup>ix</sup>	23.42 (6)
$O5^{ii}$ —Cs1—O4 <sup>v</sup>	80.16 (11)	$P1^{vi}$ —Cs2—P1 <sup>ix</sup>	180.00 (4)
$O3^{iii}$ —Cs1—O4 <sup>v</sup>	111.11 (9)	$O5^{iii}$ —Cs2—Cs1 <sup>x</sup>	135.51 (9)
$05^{iv}$ —Cs1—O4 <sup>v</sup>	155.38 (11)	$05^{\text{viii}}$ —Cs2—Cs1×	44.49 (9)
$O1^{v}$ —Cs1—O4 <sup>v</sup>	44.33 (9)	$O4^{vi}$ —Cs2—Cs1 <sup>x</sup>	47.57 (8)
$O1^{i}$ —Cs1—O4 <sup>vi</sup>	108.40 (9)	$O4^{ix}$ Cs2 Cs1 <sup>x</sup>	132.43 (8)
$O5^{ii}$ —Cs1—O4 <sup>vi</sup>	123.86 (11)	$O2^{iii}$ —Cs2—Cs1 <sup>x</sup>	51.24 (8)
O3 <sup>iii</sup> —Cs1—O4 <sup>vi</sup>	45.19 (9)	$O2^{viii}$ —Cs2—Cs1 <sup>x</sup>	128.76 (8)
$O5^{iv}$ —Cs1—O4 $^{vi}$	116.64 (11)	$O3^{vi}$ —Cs2—Cs1 <sup>x</sup>	69.65 (6)
$O1^v$ —Cs1—O4 <sup>vi</sup>	104.34 (10)	$O3^{ix}$ —Cs2—Cs1 <sup>x</sup>	110.35 (6)
$O4^{v}$ —Cs1—O4 <sup>vi</sup>	69.74 (3)	P1 <sup>vi</sup> —Cs2—Cs1 <sup>x</sup>	53.948 (17)
$O1^{i}$ —Cs1—O3 <sup>i</sup>	43.73 (9)	$P1^{ix}$ —Cs2—Cs1 <sup>x</sup>	126.052 (18)
$O5^{ii}$ —Cs1—O3 <sup>i</sup>	84.10 (10)	O5 <sup>iii</sup> —Cs2—Cs1 <sup>xi</sup>	44.49 (9)
O3 <sup>iii</sup> —Cs1—O3 <sup>i</sup>	114.61 (10)	O5 <sup>viii</sup> —Cs2—Cs1 <sup>xi</sup>	135.51 (9)
O5 <sup>iv</sup> —Cs1—O3 <sup>i</sup>	73.77 (11)	$O4^{vi}$ —Cs2—Cs1 <sup>xi</sup>	132.43 (8)
O1 <sup>v</sup> —Cs1—O3 <sup>i</sup>	69.13 (9)	$O4^{ix}$ —Cs2—Cs1 <sup>xi</sup>	47.57 (8)
$O4^v$ —Cs1—O3 <sup>i</sup>	112.88 (9)	O2 <sup>iii</sup> —Cs2—Cs1 <sup>xi</sup>	128.76 (8)
$O4^{vi}$ — $Cs1$ — $O3^i$	151.03 (9)	O2 <sup>viii</sup> —Cs2—Cs1 <sup>xi</sup>	51.24 (8)
O1 <sup>i</sup> —Cs1—O2 <sup>vii</sup>	136.30 (9)	O3 <sup>vi</sup> —Cs2—Cs1 <sup>xi</sup>	110.35 (6)
O5 <sup>ii</sup> —Cs1—O2 <sup>vii</sup>	77.26 (10)	$O3^{ix}$ —Cs2—Cs1 <sup>xi</sup>	69.65 (6)
O3 <sup>iii</sup> —Cs1—O2 <sup>vii</sup>	72.97 (9)	$P1^{vi}$ —Cs2—Cs $1^{xi}$	126.052 (17)
O5 <sup>iv</sup> —Cs1—O2 <sup>vii</sup>	67.31 (10)	$P1^{ix}$ —Cs2—Cs $1^{xi}$	53.948 (17)
O1 <sup>v</sup> —Cs1—O2 <sup>vii</sup>	140.87 (9)	$Cs1^x$ — $Cs2$ — $Cs1^{xi}$	180.0
O4 <sup>v</sup> —Cs1—O2 <sup>vii</sup>	98.91 (9)	O4—P1—O1	112.7 (2)
O4 <sup>vi</sup> —Cs1—O2 <sup>vii</sup>	62.76 (9)	O4—P1—O2	112.4 (2)
$O3^{i}$ — $Cs1$ — $O2^{vii}$	139.62 (9)	O1—P1—O2	112.6 (3)
O1 <sup>i</sup> —Cs1—O5 <sup>iii</sup>	47.72 (11)	O4—P1—O3	108.5 (2)
O5 <sup>ii</sup> —Cs1—O5 <sup>iii</sup>	127.44 (7)	O1—P1—O3	104.9 (2)
O3 <sup>iii</sup> —Cs1—O5 <sup>iii</sup>	82.97 (11)	O2—P1—O3	105.1 (2)
O5 <sup>iv</sup> —Cs1—O5 <sup>iii</sup>	130.65 (5)	O4—P1—Cs1 <sup>xii</sup>	57.93 (16)
O1 <sup>v</sup> —Cs1—O5 <sup>iiii</sup>	46.61 (10)	O1—P1—Cs1 <sup>xii</sup>	56.54 (16)
O4 <sup>v</sup> —Cs1—O5 <sup>iiii</sup>	71.53 (10)	O2—P1—Cs1 <sup>xii</sup>	146.05 (15)
O4 <sup>vi</sup> —Cs1—O5 <sup>iii</sup>	86.45 (11)	O3—P1—Cs1 <sup>xii</sup>	108.83 (14)
O3 <sup>i</sup> —Cs1—O5 <sup>iii</sup>	68.44 (10)	$O4$ — $P1$ — $Cs1^{vi}$	57.03 (16)

O2 <sup>vii</sup> —Cs1—O5 <sup>iii</sup>	149.01 (10)	O1—P1—Cs1 <sup>vi</sup>	160.89 (15)
$O1^{i}$ — $Cs1$ — $O2^{vi}$	150.96 (9)	$O2$ — $P1$ — $Cs1^{vi}$	63.79 (17)
$O5^{ii}$ — $Cs1$ — $O2^{vi}$	81.37 (10)	O3—P1—Cs1 <sup>vi</sup>	93.97 (14)
O3 <sup>iii</sup> —Cs1—O2 <sup>vi</sup>	80.78 (9)	Cs1 <sup>xii</sup> —P1—Cs1 <sup>vi</sup>	114.88 (3)
O5 <sup>iv</sup> —Cs1—O2 <sup>vi</sup>	107.78 (10)	O4—P1—Cs1 <sup>xiii</sup>	115.50 (16)
$O1^{v}$ —Cs1—O2 <sup>vi</sup>	103.57 (9)	O1—P1—Cs1 <sup>xiii</sup>	47.43 (16)
$O4^{v}$ —Cs1—O2 <sup>vi</sup>	59.38 (9)	O2—P1—Cs1 <sup>xiii</sup>	132.10 (16)
$O4^{vi}$ —Cs1—O2 <sup>vi</sup>	42.57 (9)	O3—P1—Cs1 <sup>xiii</sup>	58.82 (13)
$O3^{i}$ —Cs1—O2 <sup>vi</sup>	164.55 (8)	Cs1 <sup>xii</sup> —P1—Cs1 <sup>xiii</sup>	67.79 (2)
$O2^{\text{vii}}$ —Cs1— $O2^{\text{vi}}$	40.78 (11)	$Cs1^{vi}$ —P1—Cs1 <sup>xiii</sup>	149.62 (3)
$05^{iii}$ Cs1 $02^{vi}$	117 14 (9)	04—P1—Cs2 <sup>xiv</sup>	48 76 (16)
$01^{i}$ Cs1 $02^{i}$	127 56 (6)	$O1$ — $P1$ — $Cs2^{xiv}$	116 25 (18)
$05^{ii}$ Cs1 $-01^{vii}$	45 60 (9)	$\Omega^2 - P1 - Cs^{2xiv}$	131 13 (17)
$03^{iii}$ Cs1 $01^{vii}$	104 76 (9)	$O_2 = P_1 = C_{s2}^{xiv}$	60.45(15)
$O5^{iv}$ $Cs1$ $O1^{vii}$	45 34 (10)	$C_{s}1^{xii}$ P1 $C_{s}2^{xiv}$	70.21(2)
$O_{1}^{v}$ $C_{s1}$ $O_{1}^{vii}$	127.89(7)	$C_{s1}^{vi}$ P1 $C_{s2}^{xiv}$	70.21(2) 70.71(2)
$O_1 = C_{s1} = O_1^{vii}$	127.89(7) 110.70(0)	$C_{S1} \xrightarrow{-1} 1 \xrightarrow{-C_{S2}} C_{S1}$	70.71(2) 83.12(2)
O4 = Cs1 = O1	110.79(9) 102.60(0)	$CS1 \longrightarrow I \longrightarrow CS2$	63.12(2)
$O_{2i} = C_{21} = O_{1}^{iii}$	103.09 (9)	$O4$ $P1$ $Cs1^{xy}$	121.36(17)
$O_{3} = C_{3} = O_{1} = O_{1}$	101.90 (9)	$O_1 - P_1 - C_2 I_2$	52.45(17)
$02^{\text{vm}}$ Cs1 $01^{\text{vm}}$	41.17(8)	$O2$ —PI—CsI $^{\text{AV}}$	52.45 (16)
$O_{2}$	169.82 (10)	$O_3 - P_1 - C_{S_1}$	129.64 (16)
$02^{\text{H}}$	/1.25 (8)	$C_{SI}^{AA} = PI = C_{SI}^{AA}$	102.09 (3)
$05^{\text{m}}$ $Cs2$ $05^{\text{m}}$	180.00 (15)	$C_{SI} = PI = C_{SI}$	107.94 (3)
$05^{\text{m}}$ $Cs2$ $04^{\text{m}}$	96.92 (11)	$CsI^{xm}$ $PI$ $CsI^{xv}$	100.53 (3)
$O5^{\text{vm}}$ —Cs2—O4 <sup>vi</sup>	83.08 (11)	$Cs2^{xiv}$ —P1— $Cs1^{xv}$	169.71 (3)
$O5^{m}$ —Cs2—O4 <sup>ix</sup>	83.08 (11)	$P1 - O1 - Cs1^{xin}$	111.82 (19)
$O5^{vin}$ — $Cs2$ — $O4^{ix}$	96.92 (11)	$P1 - Cs1^{xn}$	100.98 (19)
$O4^{v_1}$ — $Cs2$ — $O4^{i_x}$	180.00 (14)	$Cs1^{xm}$ — $O1$ — $Cs1^{xm}$	85.50 (11)
$O5^{iii}$ — $Cs2$ — $O2^{iii}$	92.72 (11)	$P1 - O1 - Cs1^{xv}$	97.16 (19)
O5 <sup>viii</sup> —Cs2—O2 <sup>iii</sup>	87.28 (11)	Cs1 <sup>xiii</sup> —O1—Cs1 <sup>xv</sup>	131.82 (13)
$O4^{vi}$ — $Cs2$ — $O2^{iii}$	64.26 (10)	Cs1 <sup>xii</sup> —O1—Cs1 <sup>xv</sup>	126.80 (10)
O4 <sup>ix</sup> —Cs2—O2 <sup>iii</sup>	115.74 (10)	P1—O2—Cs $2^{xvi}$	129.92 (19)
O5 <sup>iii</sup> —Cs2—O2 <sup>viii</sup>	87.28 (11)	$P1 - O2 - Cs1^{xv}$	107.01 (19)
O5 <sup>viii</sup> —Cs2—O2 <sup>viii</sup>	92.72 (11)	$Cs2^{xvi}$ — $O2$ — $Cs1^{xv}$	107.25 (10)
$O4^{vi}$ — $Cs2$ — $O2^{viii}$	115.74 (10)	P1—O2—Cs1 <sup>vi</sup>	93.40 (18)
$O4^{ix}$ — $Cs2$ — $O2^{viii}$	64.26 (10)	$Cs2^{xvi}$ — $O2$ — $Cs1^{vi}$	83.54 (9)
O2 <sup>iii</sup> —Cs2—O2 <sup>viii</sup>	180.0	Cs1 <sup>xv</sup> —O2—Cs1 <sup>vi</sup>	139.22 (11)
O5 <sup>iii</sup> —Cs2—O3 <sup>vi</sup>	105.11 (9)	P1—O3—Cs1 <sup>xi</sup>	157.2 (2)
$O5^{viii}$ — $Cs2$ — $O3^{vi}$	74.89 (9)	P1—O3—Cs1 <sup>xiii</sup>	97.79 (15)
$O4^{vi}$ — $Cs2$ — $O3^{vi}$	43.86 (9)	Cs1 <sup>xi</sup> —O3—Cs1 <sup>xiii</sup>	81.91 (8)
O4 <sup>ix</sup> —Cs2—O3 <sup>vi</sup>	136.14 (9)	P1-O3-Cs2 <sup>xiv</sup>	96.13 (17)
O2 <sup>iii</sup> —Cs2—O3 <sup>vi</sup>	106.96 (9)	Cs1 <sup>xi</sup> —O3—Cs2 <sup>xiv</sup>	106.39 (10)
O2 <sup>viii</sup> —Cs2—O3 <sup>vi</sup>	73.04 (9)	Cs1 <sup>xiii</sup> —O3—Cs2 <sup>xiv</sup>	99.49 (9)
O5 <sup>iii</sup> —Cs2—O3 <sup>ix</sup>	74.89 (9)	$P1$ — $O4$ — $Cs2^{xiv}$	110.6 (2)
O5 <sup>viii</sup> —Cs2—O3 <sup>ix</sup>	105.11 (9)	P1—O4—Cs1 <sup>xii</sup>	99.74 (19)
O4 <sup>vi</sup> —Cs2—O3 <sup>ix</sup>	136.14 (9)	Cs2 <sup>xiv</sup> —O4—Cs1 <sup>xii</sup>	87.54 (10)
O4 <sup>ix</sup> —Cs2—O3 <sup>ix</sup>	43.86 (9)	P1—O4—Cs1 <sup>vi</sup>	101.11 (19)
O2 <sup>iii</sup> —Cs2—O3 <sup>ix</sup>	73.04 (9)	$Cs2^{xiv}$ —O4— $Cs1^{vi}$	88.48 (10)
	\[         \]     \[         \[         \]     \[		

O2 <sup>viii</sup> —Cs2—O3 <sup>ix</sup>	106.96 (9)	$Cs1^{xii}$ —O4— $Cs1^{vi}$	158.85 (12)
O3 <sup>vi</sup> —Cs2—O3 <sup>ix</sup>	180.0	Cs2 <sup>xvi</sup> —O5—Cs1 <sup>xvii</sup>	91.74 (11)
$O5^{iii}$ — $Cs2$ — $P1^{vi}$	103.74 (8)	Cs2 <sup>xvi</sup> —O5—Cs1 <sup>xviii</sup>	110.45 (13)
$O5^{viii}$ — $Cs2$ — $P1^{vi}$	76.26 (8)	Cs1 <sup>xvii</sup> —O5—Cs1 <sup>xviii</sup>	85.42 (11)
$O4^{vi}$ — $Cs2$ — $P1^{vi}$	20.65 (7)	$Cs2^{xvi}$ — $O5$ — $Cs1^{xi}$	86.75 (11)
$O4^{ix}$ — $Cs2$ — $P1^{vi}$	159.35 (7)	$Cs1^{xvii}$ — $O5$ — $Cs1^{xi}$	138.66 (14)
$O2^{iii}$ — $Cs2$ — $P1^{vi}$	83.75 (7)	$Cs1^{xviii}$ —O5— $Cs1^{xi}$	133.48 (14)
O4—P1—O1—Cs1 <sup>xiii</sup>	104.4 (2)	O4—P1—O3—Cs1 <sup>xi</sup>	163.2 (5)
O2—P1—O1—Cs1 <sup>xiii</sup>	-127.1 (2)	O1—P1—O3—Cs1 <sup>xi</sup>	-76.1 (5)
O3—P1—O1—Cs1 <sup>xiii</sup>	-13.4 (2)	O2—P1—O3—Cs1 <sup>xi</sup>	42.8 (5)
Cs1 <sup>xii</sup> —P1—O1—Cs1 <sup>xiii</sup>	89.52 (19)	$Cs1^{xii}$ —P1—O3— $Cs1^{xi}$	-135.3 (4)
$Cs1^{vi}$ —P1—O1— $Cs1^{xiii}$	158.0 (4)	$Cs1^{vi}$ —P1—O3— $Cs1^{xi}$	106.7 (5)
$Cs2^{xiv}$ —P1—O1— $Cs1^{xiii}$	50.6 (2)	$Cs1^{xiii}$ —P1—O3— $Cs1^{xi}$	-87.6 (5)
$Cs1^{xv}$ —P1—O1— $Cs1^{xiii}$	-140.7 (2)	$Cs2^{xiv}$ —P1—O3— $Cs1^{xi}$	171.9 (5)
O4—P1—O1—Cs1 <sup>xii</sup>	14.9 (2)	$Cs1^{xv}$ —P1—O3— $Cs1^{xi}$	-10.6 (6)
O2—P1—O1—Cs1 <sup>xii</sup>	143.33 (17)	O4—P1—O3—Cs1 <sup>xiii</sup>	-109.2 (2)
O3—P1—O1—Cs1 <sup>xii</sup>	-102.95 (18)	O1—P1—O3—Cs1 <sup>xiii</sup>	11.5 (2)
$Cs1^{vi}$ —P1—O1— $Cs1^{xii}$	68.5 (6)	O2—P1—O3—Cs1 <sup>xiii</sup>	130.43 (19)
$Cs1^{xiii}$ —P1—O1— $Cs1^{xii}$	-89.52 (19)	$Cs1^{xii}$ —P1—O3— $Cs1^{xiii}$	-47.68 (13)
$Cs2^{xiv}$ —P1—O1— $Cs1^{xii}$	-38.89 (16)	$Cs1^{vi}$ $P1$ $O3$ $Cs1^{xiii}$	-165.66 (8)
$Cs1^{xv}$ — $P1$ — $O1$ — $Cs1^{xii}$	129.74 (15)	$Cs2^{xiv}$ —P1—O3— $Cs1^{xiii}$	-100.49 (12)
O4—P1—O1—Cs1 <sup>xv</sup>	-114.8 (2)	$Cs1^{xv}$ —P1—O3— $Cs1^{xiii}$	77.06 (16)
O2—P1—O1—Cs1 <sup>xv</sup>	13.6 (2)	O4-P1-O3-Cs2 <sup>xiv</sup>	-8.7 (2)
O3—P1—O1—Cs1 <sup>xv</sup>	127.31 (17)	O1—P1—O3—Cs2 <sup>xiv</sup>	112.02 (19)
$Cs1^{xii}$ $P1$ $O1$ $Cs1^{xv}$	-129.74 (15)	O2—P1—O3—Cs2 <sup>xiv</sup>	-129.08 (19)
$Cs1^{vi}$ —P1—O1— $Cs1^{xv}$	-61.3 (6)	$Cs1^{xii}$ —P1—O3— $Cs2^{xiv}$	52.81 (11)
$Cs1^{xiii}$ —P1—O1— $Cs1^{xv}$	140.7 (2)	$Cs1^{vi}$ $P1$ $O3$ $Cs2^{xiv}$	-65.17 (8)
$Cs2^{xiv}$ —P1—O1— $Cs1^{xv}$	-168.64 (4)	$Cs1^{xiii}$ —P1—O3— $Cs2^{xiv}$	100.49 (12)
O4—P1—O2—Cs2 <sup>xvi</sup>	-115.2 (3)	$Cs1^{xv}$ —P1—O3— $Cs2^{xiv}$	177.55 (6)
$O1$ — $P1$ — $O2$ — $Cs2^{xvi}$	116.2 (3)	$O1$ — $P1$ — $O4$ — $Cs2^{xiv}$	-105.7 (2)
$O3$ — $P1$ — $O2$ — $Cs2^{xvi}$	2.6 (3)	$O2$ —P1—O4—Cs $2^{xiv}$	125.8 (2)
$Cs1^{xii}$ —P1—O2— $Cs2^{xvi}$	179.36 (6)	O3—P1—O4—Cs2 <sup>xiv</sup>	10.0 (2)
$Cs1^{vi}$ —P1—O2— $Cs2^{xvi}$	-84.4 (2)	$Cs1^{xii}$ —P1—O4— $Cs2^{xiv}$	-91.03 (17)
$Cs1^{xiii}$ —P1—O2— $Cs2^{xvi}$	63.9 (3)	$Cs1^{vi}$ —P1—O4— $Cs2^{xiv}$	92.57 (19)
$Cs2^{xiv}$ —P1—O2— $Cs2^{xvi}$	-61.2 (3)	$Cs1^{xiii}$ —P1—O4— $Cs2^{xiv}$	-53.5 (2)
$Cs1^{xv}$ —P1—O2— $Cs2^{xvi}$	131.3 (3)	$Cs1^{xv}$ —P1—O4— $Cs2^{xiv}$	-175.58 (5)
$O4-P1-O2-Cs1^{xv}$	113.4 (2)	O1—P1—O4—Cs1 <sup>xii</sup>	-14.7 (2)
$O1$ — $P1$ — $O2$ — $Cs1^{xv}$	-15.1 (2)	O2-P1-O4-Cs1 <sup>xii</sup>	-143.19 (18)
O3—P1—O2—Cs1 <sup>xv</sup>	-128.78 (17)	O3—P1—O4—Cs1 <sup>xii</sup>	101.07 (18)
$Cs1^{xii}$ —P1—O2— $Cs1^{xv}$	48.0 (3)	$Cs1^{vi}$ —P1—O4— $Cs1^{xii}$	-176.4 (2)
$Cs1^{vi}$ —P1—O2— $Cs1^{xv}$	144.24 (16)	$Cs1^{xiii}$ —P1—O4— $Cs1^{xii}$	37.52 (18)
$Cs1^{xiii}$ —P1—O2— $Cs1^{xv}$	-67.4 (2)	$Cs2^{xiv}$ —P1—O4— $Cs1^{xii}$	91.03 (17)
$Cs2^{xiv}$ —P1—O2— $Cs1^{xv}$	167.51 (6)	$Cs1^{xv}$ —P1—O4— $Cs1^{xii}$	-84.55 (15)
O4— $P1$ — $O2$ — $Cs1$ <sup>vi</sup>	-30.8 (2)	O1— $P1$ — $O4$ — $Cs1$ <sup>vi</sup>	161.71 (19)
O1—P1—O2—Cs1 <sup>vi</sup>	-159.38 (16)	O2—P1—O4—Cs1 <sup>vi</sup>	33.2 (2)
O3—P1—O2—Cs1 <sup>vi</sup>	86.98 (17)	O3—P1—O4—Cs1 <sup>vi</sup>	-82.53 (19)
$Cs1^{xii}$ —P1—O2— $Cs1^{vi}$	-96.2 (3)	$Cs1^{xii}$ $P1$ $O4$ $Cs1^{vi}$	176.4 (2)

$Cs1^{xiii}$ $P1$ $O2$ $Cs1^{vi}$	148.33 (11)	$Cs1^{xiii}$ —P1—O4— $Cs1^{vi}$	-146.08 (7)
$Cs2^{xiv}$ —P1—O2— $Cs1^{vi}$	23.27 (19)	$Cs2^{xiv}$ P1 O4 $Cs1^{vi}$	-92.57 (19)
$Cs1^{xv}$ —P1—O2— $Cs1^{vi}$	-144.24 (16)	$Cs1^{xv}$ —P1—O4— $Cs1^{vi}$	91.85 (15)

Symmetry codes: (i) -x+1, y+1/2, -z+1/2; (ii) x, y+1, z; (iii) -x+1/2, y+1/2, z; (iv) x-1/2, y+1, -z+1/2; (v) -x+3/2, y+1/2, z; (vi) -x+1, -y+1, -z; (vii) x-1, y+1, z; (viii) x-1/2, -y+1/2, -z; (ix) x-1, y, z; (x) x-1/2, -y+3/2, -z; (xi) -x+1/2, y-1/2, z; (xii) -x+3/2, y-1/2, z; (xiii) -x+1, y-1/2, -z+1/2; (xiv) x+1, y, z; (xv) x+1, y-1, z; (xvi) x+1/2, -y+1/2, -z; (xvii) x, y-1, z; (xviii) x+1/2, y-1, -z+1/2.

*Hydrogen-bond geometry (Å, °)* 

D—H···A	<i>D</i> —Н	H···A	$D \cdots A$	D—H…A
O2—H2····O2 <sup>xix</sup>	1.22 (1)	1.22 (1)	2.445 (7)	180 (1)
O3—H3···O4 <sup>viii</sup>	0.80 (2)	1.75 (2)	2.549 (5)	177 (6)
O5—H5A···O1 <sup>ix</sup>	0.82 (8)	1.90 (8)	2.713 (6)	175 (7)
O5— $H5B$ ···O1 <sup>xx</sup>	0.90 (8)	1.82 (8)	2.725 (6)	176 (7)

Symmetry codes: (viii) x-1/2, -y+1/2, -z; (ix) x-1, y, z; (xix) -x+2, -y, -z; (xx) x-1/2, y, -z+1/2.