The caesium phosphates $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2(\text{H}_2\text{O})_2$, $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2$, $\text{Cs}_4\text{P}_2\text{O}_7(\text{H}_2\text{O})_4$, and $\text{CsPO}_3$

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Abstract
The caesium phosphates $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2(\text{H}_2\text{O})_2$ and $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2$ were obtained from aqueous solutions, and $\text{Cs}_4\text{P}_2\text{O}_7(\text{H}_2\text{O})_4$ and $\text{CsPO}_3$ from solid state reactions, respectively. $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2$, $\text{Cs}_4\text{P}_2\text{O}_7(\text{H}_2\text{O})_4$, and $\text{CsPO}_3$ were fully structurally characterized for the first time on basis of single-crystal X-ray diffraction data recorded at $-173$ °C. Monoclinic $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2$ ($Z=2$, $C2/m$) represents a new structure type and comprises hydrogen phosphate groups involved in the formation of a strong non-symmetrical hydrogen bond (accompanied by a disordered H atom over a twofold rotation axis) and a very strong symmetric hydrogen bond (with the H atom situated on an inversion centre) with symmetry-related neighbouring anions. Triclinic $\text{Cs}_4\text{P}_2\text{O}_7(\text{H}_2\text{O})_4$ ($Z=2$, $P\bar{1}$) crystallizes also in a new structure type and is represented by a diphasphate group with a P–O–P bridging angle of 128.5°. Although H atoms of the water molecules were not modelled, O···O distances point to hydrogen bonds of medium strengths in the crystal structure. $\text{CsPO}_3$ is monoclinic ($Z=4$, $P2_1/n$) and belongs to the family of $\text{catena}$-polyphosphates ($\text{MPO}_3$)$_n$ with a repetition period of 2. It is isotypic with the room-temperature modification of $\text{RbPO}_3$. The crystal structure of $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_2(\text{H}_2\text{O})_2$ was re-evaluated on the basis of single-crystal X-ray diffraction data at $-173$ °C, revealing that two adjacent hydrogen phosphate anions are connected by a very strong and non-symmetrical hydrogen bond, in contrast to the previously described symmetrical bonding situation derived from room temperature X-ray diffraction data. In the four title crystal structures, coordination numbers of the caesium cations range from 7 to 12.

Graphic abstract

Keywords  Solid state · Alkali metals · X-ray structure determination · Hydrogen bonds

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Introduction
The recent interest in the family of caesium phosphates is mainly connected with the high proton conductivity of $\text{Cs}(\text{H}_2\text{PO}_4)$ to be utilized as a potential electrolyte for intermediate temperature fuel cells [1–3] or for water electrolysis [4]. Another motivation to search for new caesium phosphates is related to acidic salts with formulae $\text{M}_x\text{H}_y(\text{AO}_4)_z$ ($\text{M}=\text{Cs}, \text{Rb}, \text{K}, \text{Na}, \text{Li}, \text{NH}_4; \text{A}=\text{S}, \text{Se}, \text{As}, \text{P}$) that likewise exhibit proton conductivity or have ferroelectric properties.
In this context, the new proton conductor Cs$_3$(H$_2$PO$_4$)·(HPO$_4$)$_2$H$_2$O (=Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$) has been characterized lately [5].

Numerous caesium phosphates have been completely structurally characterized so far, viz. the low-temperature form of Cs$_3$(PO$_4$)$_2$ [6], Cs$_3$(HPO$_4$)(H$_2$O)$_3$ [7], Cs(H$_2$PO$_4$) in its low- and room-temperature forms [8–10], as a super-protonic conductor phase [11] and in its high-pressure forms [12], Cs$_2$(H$_2$P$_2$O$_7$) [13], Cs$_3$(H$_2$P$_2$O$_7$)(H$_2$O) [14], Cs$_4$(P$_2$O$_7$) [15], Cs$_8$(P$_2$O$_7$)(H$_2$O)$_6$ [16], Cs$_5$(P$_3$O$_9$)(H$_2$O) [17], Cs$_4$(P$_3$O$_9$)$_2$(H$_2$O)$_4$ [18], and Cs$_8$(P$_8$O$_2$)(H$_2$O)$_8$ [19].

Here, we report on the crystal structure refinements of the four caesium phosphates Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$, Cs$_3$(H$_{1.5}$PO$_4$)$_2$, Cs$_3$P$_2$O$_7$(H$_2$O)$_2$, and CsPO$_3$. On the basis of high-quality single-crystal X-ray data sets recorded at −173 °C, it was possible to get full structural details for Cs$_3$(H$_{1.5}$PO$_4$)$_2$ and CsPO$_3$. Up to now, for these compounds only X-ray powder data were available from previous studies [5, 20]. In addition, the hydrogen-bonding scheme in the crystal structure of Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ [5] was re-evaluated, and the hydrous diphosphate Cs$_3$P$_2$O$_7$(H$_2$O)$_4$ is reported here for the first time.

**Results and discussion**

Results of bond valence sum (BVS) calculations [21] using the parameters provided by Brese and O’Keeffe [22] reveal values for Cs$^+$ and P atoms in all structures very close to the expected formal total valencies of +I and +V, respectively, with the highest deviation being 0.15 valence units for some P atoms (Table 1).

**Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$**

Concerning the previous single-crystal X-ray study of Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ at room temperature [5], the results of the current low-temperature study have a higher precision. However, the principal structural arrangement is the same with respect to the two refinements/models. Differences in bond lengths and angles for individual structure units between the two models are negligible and might be caused by different measurement temperatures. Selected bond lengths and angles resulting from the current refinement are collated in Table 1. Since the crystal structure of Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ has been discussed in detail, here only the main features are given. The crystal structure is built up of hydrogen phosphate tetrahedra connected through strong hydrogen bonds involving the hydrogen atoms H1 and H2 (Table 2) into undulating layers parallel (001). Under further contribution of two hydrogen-bonding interactions of medium strengths involving the water molecule (OW), a three-dimensional network is formed (Fig. 1). The two independent caesium cations are located in the voids of this arrangement and are bonded to eight (Cs1) and twelve (Cs2) O atoms (Fig. 2, Table 1).

The chief difference between the two models pertains to the very strong hydrogen bond developed between two phosphate tetrahedra involving O2 and its symmetry-related counterpart (O2···O2(−x + 1, −y, −z)) at a distance of ≈ 2.44 Å. In the previous room-temperature model [5], this hydrogen bond was suggested as being symmetric, with the H atom exactly positioned between the two O2 atoms at an inversion centre of space group Pbcn (Wyckoff position 1a). Based on difference Fourier maps obtained from the current data set (Fig. 3), which clearly revealed two symmetry-related maxima in the vicinity of the inversion centre, we modelled the corresponding H atom (H2) as being statistically disordered, resulting in a non-symmetrical O2···O2 hydrogen bond (Table 2). The bonding situation regarding such a very strong hydrogen bond between two hydrogen phosphate groups with disordered hydrogen atoms is similar as in other structures comprising tetrahedral oxoanions with OH groups, e.g. in (NH$_4$)$_2$H$_2$(PO$_4$)$_2$ [23], Tl$_2$H$_2$(AsO$_4$)$_2$ [24], or Na$_x$H$_2$(SeO$_4$)$_4$(H$_2$O)$_2$ [25].

Although the present low-temperature X-ray diffraction data for Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ clearly point to an unsymmetrical hydrogen bond O2···H2···O2(−x + 1, −y, −z) with a disordered H2 atom, it remains unclear whether this model also applies at room temperature, or whether the reported model [5] with a symmetrical hydrogen bond O2—H2—O2′ and with H2 situated at an inversion centre is correct at this temperature. Note that the O2···O2′ distance derived from the room-temperature measurement (2.445(7) Å [5]) is slightly longer than in the current low-temperature measurement (2.434(3) Å), indicating an expansion of the structure. Therefore, the likelihood of a symmetric hydrogen bond is expected to decrease with higher temperature. In the end, this question (unsymmetrical versus symmetrical hydrogen bond) can be answered without ambiguity only on basis of temperature-dependent neutron diffraction data.

**Cs$_3$(H$_{1.5}$PO$_4$)$_2$**

Cs$_3$(H$_{1.5}$PO$_4$)$_2$ was reported to exist as a dehydration product of Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ and to be stable between −50 and 275 °C. Except for unit cell parameters and space group assignment on basis of a laboratory X-ray powder study, no further structural details were given for this phase [5]. The unit cell parameters determined from polycrystalline Cs$_3$(H$_{1.5}$PO$_4$)$_2$ at 160 °C (a = 11.1693(4), b = 6.4682(2), c = 3.6 Å) were considered as relevant because a bond of this length still adds 0.04 valence units to the overall BVS.
The caesium phosphates $\text{Cs}_3(\text{H}_3\text{PO}_4)\text{(H}_2\text{O})_2$, $\text{Cs}_3(\text{H}_3\text{PO}_4)_2$, and $\text{CsPO}_3$...  

|                  | $\text{Cs}_3(\text{H}_3\text{PO}_4)\text{(H}_2\text{O})_2$ | $\text{Cs}_3(\text{H}_3\text{PO}_4)_2$ | $\text{Cs}_4\text{P}_2\text{O}_7\text{(H}_2\text{O})_4$ | $\text{CsPO}_3$ |
|------------------|-------------------------------------------------|---------------------------------|---------------------------------|-----------------|
| Cs1 OW           | 3.0975(15) $\times 2$                          | Cs1 O2                          | 3.0836(17) $\times 2$          | Cs1 O5          |
| Cs1 O4           | 3.1567(13) $\times 2$                          | Cs1 O1                          | 3.2187(13) $\times 4$          | Cs1 O1          |
| Cs1 O2           | 3.2124(13) $\times 2$                          | Cs1 O3                          | 3.4031(13) $\times 4$          | Cs1 O1          |
| Cs1 O1           | 3.4336(13) $\times 2$                          | BVS                             | 1.07                            |                 |
| BVS              | 0.95                                            |                                 |                                 |                 |
| Cs2 O3           | 3.1241(15)                                      | Cs2 O2                          | 3.1068(18)                      | Cs2 OW2         |
| Cs2 OW           | 3.1384(15)                                      | Cs2 O1                          | 3.1570(12) $\times 2$          | Cs1 O6          |
| Cs2 O1           | 3.2209(13)                                      | Cs2 O2                          | 3.2709(12) $\times 2$          | BVS 1.00        |
| Cs2 OW           | 3.2475(15)                                      | Cs2 O1                          | 3.2978(15) $\times 2$          |                 |
| Cs2 O1           | 3.3836(12)                                      | BVS                             | 1.02                            |                 |
| Cs2 O3           | 3.2626(13)                                      |                                 |                                 |                 |
| Cs2 O4           | 3.3093(13)                                      | P1 O2                           | 1.5030(15)                      | Cs2 O6          |
| Cs2 O4           | 3.3492(13)                                      | P1 O3                           | 1.5459(15)                      | Cs2 OW3         |
| Cs2 O2           | 3.3898(14)                                      | P1 O1                           | 1.5697(9) $\times 2$           | Cs2 O3          |
| Cs2 O2           | 3.3909(13)                                      | BVS                             | 4.85                            |                 |
| Cs2 OW           | 3.5057(15)                                      |                                 |                                 |                 |
| Cs2 O2           | 3.5515(14)                                      |                                 |                                 |                 |
| BVS              | 1.03                                            |                                 |                                 |                 |
| P1 O4            | 1.5102(14)                                      |                                 |                                 |                 |
| P1 O3            | 1.5184(15)                                      |                                 |                                 |                 |
| P1 O2            | 1.5431(14)                                      |                                 |                                 |                 |
| P1 O1            | 1.5942(13)                                      |                                 |                                 |                 |
| BVS              | 4.92                                            |                                 |                                 |                 |

Table 1 Selected interatomic distances/Å, angles/°, and results of BVS calculations/valence units for the four caesium phosphates

|                  | $\text{Cs}_3(\text{H}_3\text{PO}_4)\text{(H}_2\text{O})_2$ | $\text{Cs}_3(\text{H}_3\text{PO}_4)_2$ | $\text{Cs}_4\text{P}_2\text{O}_7\text{(H}_2\text{O})_4$ | $\text{CsPO}_3$ |
|------------------|-------------------------------------------------|---------------------------------|---------------------------------|-----------------|
| Cs3 OW           | 3.0642(18)                                      |                                 |                                 |                 |
| Cs3 O3           | 3.0754(18)                                      |                                 |                                 |                 |
| Cs3 O2           | 3.2289(16)                                      |                                 |                                 |                 |
| Cs3 OW           | 3.2819(19)                                      |                                 |                                 |                 |
| Cs3 OW           | 3.2979(19)                                      |                                 |                                 |                 |
| Cs3 O2           | 3.2997(15)                                      |                                 |                                 |                 |
| Cs3 O6           | 3.3313(16)                                      |                                 |                                 |                 |
| Cs3 O7           | 3.3925(14)                                      |                                 |                                 |                 |
| Cs3 OW           | 3.462(2)                                        |                                 |                                 |                 |
| BVS              | 0.95                                            |                                 |                                 |                 |
| Cs4 OW           | 3.1116(14)                                      |                                 |                                 |                 |
| Cs4 O5           | 3.1304(13)                                      |                                 |                                 |                 |
| Cs4 OW           | 3.1375(16)                                      |                                 |                                 |                 |
| Cs4 O7           | 3.2037(15)                                      |                                 |                                 |                 |
| Cs4 OW           | 3.230(2)                                        |                                 |                                 |                 |
| Cs4 OW           | 3.243(2)                                        |                                 |                                 |                 |
| Cs4 OW           | 3.2576(17)                                      |                                 |                                 |                 |
| Cs4 O1           | 3.4014(16)                                      |                                 |                                 |                 |
| Cs4 OW           | 3.507(2)                                        |                                 |                                 |                 |
| BVS              | 1.00                                            |                                 |                                 |                 |
| P1 O1            | 1.5162(18)                                      |                                 |                                 |                 |
| P1 O2            | 1.5178(16)                                      |                                 |                                 |                 |
| P1 O3            | 1.5211(15)                                      |                                 |                                 |                 |
| P1 O4            | 1.6458(16)                                      |                                 |                                 |                 |
| BVS              | 4.85                                            |                                 |                                 |                 |
| P2 O5            | 1.5073(16)                                      |                                 |                                 |                 |
| P2 O7            | 1.5196(18)                                      |                                 |                                 |                 |
$c = 7.7442(3)$ Å, $\beta = 71.822(2)$°, $V = 531.56$ Å$^3$) [5] are in good agreement with the values from the current single-crystal X-ray data at $-173$ °C (Table 3). However, the space group derived from the powder study was reported to be $C_2$ (No. 5), whereas the current refinement clearly indicates the higher $C_2/m$ space group symmetry.

The unique crystal structure of Cs$_3$(H$_{1.5}$PO$_4$)$_2$ at $-173$ °C resembles that of the corresponding dihydrate described above and comprises two Cs, one P, three O, and two H atoms in the asymmetric unit. Cs1 is situated on Wyckoff position 2$a$ (site symmetry $2/m$), Cs2, P1, O1, O2, O3 are all situated on position 4$i$ ($m$), H1 ($8j$; 1) is disordered about a twofold rotation axis, and H3 is situated on Wyckoff position 2$b$ ($2/m$).

The P–O bond lengths distribution is typical for a hydrogen phosphate anion, with the P–OH bonds (involving O3 and O1) considerably longer (average 1.562 Å) than the P–O2 bond of 1.503 Å. Whereas the latter oxygen atom is not engaged in hydrogen bonding, each of the OH groups is involved in very strong to strong hydrogen bonding with its symmetry-related counterpart generated through a $2/m$ operation and a twofold rotation axis, respectively. Individual phosphate tetrahedra are connected through a very strong (O···O = 2.458(2) Å) and symmetrical hydrogen bond O3–H3–O3($-x + 1$, $y$, $-z$) (Table 2) with H3 at a $2/m$ position to form a dimer with composition {H(HPO$_4$)$_2$}$^{3-}$. Adjacent dimers are linked through additional strong hydrogen bonds (O···O = 2.55 Å) involving the disordered H1 atom (O1–H1···O1($-x + 1$, $y$, $-z - 1$) into zig-zag [001] chains situated at $x \approx 0$, $y \approx 0.5$ (Fig. 4).

In comparison with hydrated Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ where the very short hydrogen bond is unsymmetrical and associated with disorder of the hydrogen atom, the bonding situation of the hydrogen phosphate tetrahedron is different in Cs$_3$(H$_{1.5}$PO$_4$)$_2$. As noted above, the hydrogen bond is symmetrical as revealed by difference Fourier maps, which clearly show a maximum at the inversion centre in-between the two symmetry-related oxygen atoms O1 (Fig. 5). However, it has to be noted that the electron density about hydrogen atoms is diffuse. Thus, even for a perfectly determined electron density, an H atom disordered about the $2/m$ position may result in a single maximum, if the disordered atoms are close to said position. In consequence, as previously, only neutron diffraction studies can unambiguously demonstrate the correctness of this model, since neutrons diffract at the nucleus.

### Table 1 (continued)

| Compound                      | P2   | O6     | $d$(O=P) | BVS     |
|-------------------------------|------|--------|----------|---------|
| Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ |      |        |          |         |
| Cs$_3$(H$_{1.5}$PO$_4$)$_2$    |      |        |          |         |
| Cs$_3$P$_2$O$_7$(H$_2$O)$_4$   |      |        |          |         |
| CsPO$_3$                      |      |        |          |         |

### Table 2 Details of hydrogen bonding/Å, °

| Compound                      | D—H  | A     | $d$(D—H) | $d$(H···A) | $d$(D···A) | $\angle$(D—H···A) |
|-------------------------------|------|-------|----------|------------|------------|------------------|
| Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ | Ow Hw1 | O3   | 0.85(3)  | 1.91(3)    | 2.696(2)   | 153(4)          |
| Cs$_3$(H$_{1.5}$PO$_4$)$_2$    | O1 H1 | O1   | 0.89(3)  | 1.71(2)    | 2.5513(16) | 156(4)          |
| Cs$_3$(H$_{1.5}$PO$_4$)$_2$    | O3 H3 | O3   | 1.2288(16) | 1.2288(16) | 2.458(2)   | 180             |

*All distances <3.2 Å were considered*
The two caesium cations are situated between the hydrogen-bonded chains (Fig. 6). Each Cs1 symmetrically links four chains; it exhibits a coordination number of 10 in form of a distorted hexadecahedron [26]. Cs1 is bonded to two (non-H atom bearing) O3 atoms of two neighbouring chains with the shortest Cs–O bonds (3.07 Å) observed for this polyhedron, to four (disordered H atom bearing) symmetrically related O1 atoms at longer distances (3.22 Å), and to another four (H atom bearing) O3 atoms at the longest distance (3.41 Å). Each Cs2 likewise links four chains and is surrounded by eight O atoms in the shape of a distorted hexagonal bipyramid. The two shortly bonded O atoms O3 and O2 (d(Cs–O) ≈ 3.05 Å) define the axial O atoms, and the symmetrically related three pairs of O1 and O2 atoms define the six equatorial atoms with bond lengths ranging from 3.16 to 3.30 Å (Table 1).

**Cs₄P₂O₇(H₂O)₄**

In the crystal structure of Cs₄P₂O₇(H₂O)₄ (Fig. 7), isolated diphosphate anions are organised in layers parallel (010), thereby sandwiching adjacent layers composed of caesium cations (Cs3, Cs4) and the four water molecules along the [010] direction. The remaining two caesium cations, Cs1 and Cs2, are situated in-between individual diphosphate groups in the anionic layers.

The diphosphate anion has a staggered conformation with a P–O–P angle of 128.49(10)°. Characteristic for condensed phosphate anions [27], the two P–O bond lengths to the bridging O atom are significantly longer (1.6350(13) and 1.6458(16) Å) than the terminal P–O bond lengths (averaged values 1.518 (P1) and 1.516 (P2) Å) for the two tetrahedra of the anion. The dihedral angle between the atoms of the “backbone” of the anion (O3–P1–O4; O4–P2–O7) and the P···P distance amount to 43.23(12)° and 2.9549(8) Å, respectively. All these values are in good agreement with those of the anions of the other known hydrated alkali diphosphates, viz. Na₄P₂O₇(H₂O)₁₀ [28] (staggered conformation; average P–O terminal bond length 1.523 Å, bridging P–O 1.612 Å, P–O–P angle 130.2°; dihedral angle within the backbone 42.0°, P···P distance 2.925 Å) and K₄P₂O₇(H₂O)₃ [29] (staggered conformation; 1.503, 1.636 Å, P–O–P angle 130.3°, 25.8°, P···P distance 2.968 Å).

The coordination numbers of the four caesium cations in Cs₄P₂O₇(H₂O)₄ range from eight to ten. According to their location either in the diphosphate layer or in the water-containing layer, the cations display different coordination environments. Cs1 (CN = 8) is bonded to seven O atoms...
Fig. 2 The crystal structure of Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ in a projection along [100]. Displacement ellipsoids and colour codes are as in Fig. 1; Cs1 is given in dark blue, Cs2 in turquoise.

Fig. 3 a Difference Fourier map around symmetry-related O2 atoms (red points) on basis of a model with omission of the respective H atoms; the two maxima related to electron densities of the disordered H atoms are discernible. b $F_{\text{obs}}$ map with H atoms (pale pink dots). The sections are centred on the inversion centre at ($\frac{1}{2}$, 0, 0) and pass through the O2 atom. The width and height of the plots show 3 Å. Contours (solid: positive, dotted: negative, dashed: zero) are drawn at multiples of a 0.05 e$^{-}$/Å$^3$ and b 0.5 e$^{-}$/Å$^3$ (colour figure online).
The caesium phosphates $\text{Cs}_3(\text{H}_3\text{PO}_4)_2(\text{H}_2\text{O})_2$, $\text{Cs}_3(\text{H}_3\text{PO}_4)_2$, ... from three neighbouring diphosphate groups and to one water molecule in the adjacent layer, and Cs2 is bonded to eight O atoms from three diphosphate groups and to two water molecules. On the other hand, Cs3 and Cs4 each have six water molecules and three atoms from two and three diphosphate groups, respectively, as bonding partners. The four water molecules are either bonded to four (in case of OW1, OW2, OW3) or to three (OW4) caesium cations. Although H atoms of water molecules could not be located from the current data set, O···O distances between water O atoms and phosphate O atoms in the range 2.682–2.760 Å indicate hydrogen-bonding interactions of medium strengths (Table 2) that help to consolidate the crystal packing.

### Table 3 Details of data collections and structure refinements for caesium phosphates

| Compound                      | Cs$_3$(H$_3$PO$_4$)$_2$(H$_2$O)$_2$ | Cs$_3$(H$_3$PO$_4$)$_2$ | Cs$_3$P$_2$O$_7$(H$_2$O)$_4$ | CsPO$_3$ |
|-------------------------------|-----------------------------------|-------------------------|-----------------------------|-----------|
| Diffractometer                | —Bruker APEX2—                    | —                       | —                           | —         |
| Radiation; λ/Å                 | —MoK$_\alpha$; 0.71073—           | —                       | —                           | —         |
| Temperature °C                | —173—                             | —                       | —                           | —         |
| Crystal dimensions/mm$^3$     | 0.09×0.04×0.01                    | 0.15×0.11×0.02          | 0.32×0.12×0.02              | 0.05×0.03×0.01 |
| Crystal description           | colourless plate                  | colourless plate        | colourless plate            | colourless fragment |
| Space group                   | $P_{bca}$                         | $C2/m$                  | $P1$                        | $P2_1/n$  |
| Formula units Z               | 4                                 | 2                       | 2                           | 4         |
| $a$/Å                         | 7.4370(3)                         | 11.085(2)               | 6.5795(3)                   | 12.6162(11) |
| $b$/Å                         | 11.2832(4)                        | 6.3469(12)              | 10.4873(5)                  | 4.2932(4)  |
| $c$/Å                         | 14.7824(5)                        | 7.7038(15)              | 11.0115(5)                  | 6.7575(6)  |
| $a$°                           | 90                                | 90                      | 77.2551(16)                 | 90        |
| $\beta$°                      | 90                                | 108.578(3)              | 89.1014(17)                 | 90        |
| $\gamma$°                     | 90                                | 108.578(3)              | 89.1014(17)                 | 90        |
| $V$/Å$^3$                     | 1240.44(8)                        | 513.76(17)              | 712.04(6)                   | 363.96(6)  |
| Formula weight                | 627.7                             | 591.7                   | 777.6                       | 211.9     |
| $\mu$/mm$^{-1}$               | 9.058                             | 10.909                  | 10.422                      | 10.427    |
| X-ray density/g cm$^{-3}$     | 3.361                             | 3.825                   | 3.626                       | 3.867     |
| Range $\theta_{\text{min}}$–$\theta_{\text{max}}$° | 2.76–35.12                     | 2.79–40.36              | 1.90–35.05                  | 3.25–32.61 |
| $h$                           | $-11$ → $11$                      | $-16$ → $20$            | $-10$ → $10$                | $-19$ → $19$ |
| $k$                           | $-17$ → $18$                      | $-11$ → $11$            | $-16$ → $16$                | $-6$ → $6$   |
| $l$                           | $-23$ → $22$                      | $-14$ → $14$            | $-17$ → $17$                | $-10$ → $10$ |
| Measured reflections         | 53,698                            | 7248                    | 29,308                      | 8987      |
| Independent reflections      | 2643                              | 1736                    | 6253                        | 1396      |
| Obs. reflections [$I > 3\sigma(I)$] | 2512                             | 1632                    | 5811                        | 1380      |
| $R_I$                         | 0.025                             | 0.024                   | 0.032                       | 0.032     |
| Coeff. of transm. $T_{\text{min}}$–$T_{\text{max}}$ | 0.65; 0.91                   | 0.13; 0.58              | 0.24; 0.81                   | 0.005; 0.008 |
| Ext. coeff. [40]              | 1140(80)                          | 230(19)                 | 560(40)                     | –         |
| Number of parameters         | 86                                | 43                      | 155                         | 47        |
| $\Delta e_{\text{max}}$, $\Delta e_{\text{min}} / \ell$ Å$^{-3}$ | 0.53; –0.50                    | 0.91; –0.87             | 1.47; –0.78                   | 0.99; –1.32 |
| $R(F > 3\sigma(F))$, $wR2(F \text{ all})$ | 0.0140; 0.0266               | 0.0128; 0.0395          | 0.0168; 0.0274                | 0.0263; 0.0392 |
| Goof                          | 1.99                              | 1.21                    | 1.56                         | 1.34      |
| CSD number                    | 2015035                           | 2015034                 | 2015032                     | 2015033   |

### CsPO$_3$

Corbridge reported crystallographic data of CsPO$_3$ and other alkali long-chain polyphosphates of formula $(\text{MPO}_3)_n$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$), showing that the Rb and

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The term polyphosphate is established in the literature [27] but bears some ambiguity. In a strict sense, “poly” could describe any phosphate with a large number of, yet not exclusively containing $Q^2$ phosphate groups, where the number (here 2) designates the vertices of a $\text{PO}_4$ tetrahedron that are shared with a neighbouring $\text{PO}_4$ tetrahedron. The prefix “meta” conveys that there are exclusively $Q^2$ phosphate groups in the crystal structure, which is obviously true for all $(\text{MPO}_3)_n$ compounds. Hence, these compounds are also referred to as catena-metaphosphates.
Cs catena-polyphosphates crystallize isotypically in space group type $P2_1/n$ [20]. The crystal structure of the corresponding room-temperature modification of RbPO$_3$ was subsequently determined [29] and later re-examined twice [30, 31]. The given lattice parameters from the first study of CsPO$_3$ at room temperature ($a = 12.71$, $b = 4.32$, $c = 6.99$ Å, $\beta = 83^\circ$ [20]) are in good agreement with the current low-temperature data (Table 3, with $\beta > 90^\circ$ according to convention). Next to CsPO$_3$, TIPO$_3$ is so far the only other known catena-polyphosphate crystallizing isotypically with the RT-form of RbPO$_3$. However, crystallographic details of the thallium phase are restricted to lattice parameter and an indexed powder diffractogram [32].

The crystal structure of CsPO$_3$ (Fig. 8) comprises a polyphosphate chain extending parallel to [010], with a repeating unit of two phosphate tetrahedra. The bond lengths distribution is typical for polyphosphate chains [27], with two short P—O distances (average 1.486 Å) to terminal O atoms (O$_2$, O$_3$) and two considerably longer P-O distances (average 1.616 Å) to bridging O atoms (O$_1$ and O$_1(-x + 1/2$,

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**Fig. 4** Hydrogen-bonded chains of hydrogen tetrahedra in the crystal structure of Cs$_3$(H$_{1.5}$PO$_4$)$_2$, viewed along [010]. Displacement ellipsoids and colour codes are as in Fig. 1.

**Fig. 5** a Difference Fourier map around symmetry-related O$_3$ atoms (red points) on basis of a model with omission of the respective H atoms, showing one maximum situated at the 2/m position related to electron density of an ordered H atom; b $F_{o-h}$ map with H atom (pale pink dot). The plots represent $y=0$ sections centred around $(1/2, 0, 0)$ and show 3 Å in the $x$- and $z$-directions. Contours (solid: positive, dotted: negative, dashed: zero) are drawn at multiples of a 0.05 e$^-$/Å$^3$ and b 0.5 e$^-$/Å$^3$ (colour figure online).
The caesium phosphates $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_{2}(\text{H}_2\text{O})_2$, $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_{2}$,…

Fig. 6 The crystal structure of $\text{Cs}_3(\text{H}_{1.5}\text{PO}_4)_{2}$, in a projection along [001]. Displacement ellipsoids and colour codes are as in Fig. 2.

Fig. 7 The crystal structure of $\text{Cs}_4\text{P}_2\text{O}_7(\text{H}_2\text{O})_4$ in a projection along [100]. Displacement ellipsoids and colour codes are as in Fig. 2. The inset shows the diphosphate group with atom labelling.
y − 1/2, − z + 1/2). The Cs cations are situated in-between the chains and exhibit a coordination number of 7 with a monocapped prism as coordination polyhedron; Cs−O distances range from 3.03 to 3.37 Å (Table 1).

The program compstru [33], available at the Bilbao Crystallographic Server [34], was employed for a quantitative structural comparison of the isotypic CsPO₃ and RbPO₃ structures. For that purpose, the current low-temperature structure data of CsPO₃ and the room-temperature structure data of RbPO₃ were used, neglecting the effect of different measurement temperatures. The comparison revealed a close structural similarity between the structures. The degree of lattice distortion is 0.0193, and the distances between the atomic positions of paired atoms are 0.0211 Å for Cs/Rb, 0.0658 Å for P1, 0.0836 Å for O1, 0.1244 Å for O2, and 0.1340 Å for O3. The arithmetic mean of all distances between paired atoms is 0.0858 Å, and the measure of similarity is 0.042.

Conclusion

The crystal structures of the four caesium phosphates Cs₃(H₁.₅PO₄)₂(H₂O)₂, Cs₅(H₁.₅PO₄)₂, Cs₄P₂O₇(H₂O)₄, and CsPO₃ were refined from low-temperature X-ray diffraction data at −173 °C. Although for the two hydrogen phosphates Cs₃(H₁.₅PO₄)₂(H₂O)₂ and Cs₅(H₁.₅PO₄)₂ all hydrogen atoms could clearly be located from difference Fourier maps, an uncertainty regarding the hydrogen-bonding situation between symmetry-related hydrogen phosphate tetrahedra remains. Future neutron diffraction studies are definitely required to evidence the correctness of the structure models, here in terms of the corresponding H atom positions. Neutron diffraction data may also help to determine the H atom positions of the water molecules in hydrous Cs₄P₂O₇(H₂O)₄, which was not possible on basis of the current X-ray data. However, O···O distances involving the water molecules indicate the presence of two hydrogen-bonding interactions for each of the water molecules.

Experimental

Preparation

Crystals of Cs₃(H₁.₅PO₄)₂ were isolated from a batch intended to produce Cs₂(HPO₄). To diluted phosphoric acid (≈ 5%wt), an aqueous solution of Cs₂CO₃ was added in the molar ratio 1:1. The mixture was carefully evaporated until dryness and kept in an oven at 130 °C for one night. Colourless plate-like crystals were isolated from the hygroscopic product that also contained bulky crystals of Cs₂(HPO₄). After longer contact with ambient humidity at room temperature (about 2 days), crystals of the hydrate phase Cs₃(H₁.₅PO₄)₂(H₂O)₂ were subsequently isolated from the original reaction product.
Crystals of Cs₃P₂O₇(H₂O)₄ were isolated from a batch intended to produce anhydrous Cs₂P₂O₇ from solid state reactions. Cs₃P₂O₇ was described as an intermediate product during thermal treatment of Cs₃(H₁.₅PO₄)₃(H₂O)₂ [5] or Cs₅(HPO₄)₂(H₂O)₂ and was reported to be polymorphic [35]. Cs₂CO₃ and (NH₄)₂HPO₄ were mixed in equimolar amounts, ground and placed in a porcelain crucible that was heated from room temperature to 950 °C within 3 h, kept at that temperature for 4 h and cooled to room temperature by turning off the furnace. Colourless plates of the tetrahydrate were harvested from the bulk product.

CsPO₃ was prepared by mixing a diluted solution of phosphoric acid (≈ 5% w/w) and an aqueous solution of Cs₂CO₃ in the molar ratio of 2:1. The mixture was subsequently warmed until dryness and heated within 2 h to 750 °C, kept at that temperature for 2 h, cooled within 10 h to 300 °C and then quickly removed from the furnace.

**Structure determination**

All crystals were hygroscopic and thus were embedded in perfluorinated oil for protection. Diffraction experiments on optically preselected crystals followed standard measurement procedures with corresponding software packages for data collection and data reduction [36]. All data sets were corrected for absorption effects by using the semiempirical multi-scan method [37]. The crystal structures were solved by charge flipping [38] and refined with JANA2006 [39].

All H atoms in the structures of Cs₃(H₁.₅PO₄)₂ and Cs₅(H₁.₅PO₄)₃(H₂O)₂ were located from difference Fourier maps and were refined with O–H distance constraints of 0.86(2) Å, except for the symmetrical hydrogen bond in Cs₅(H₁.₅PO₄)₃ where the H atom is located on Wyckoff position 2b (2/m). H atoms of the water molecules could not be localized reliably for Cs₅P₂O₇(H₂O)₄ and therefore are not included in the final crystal structure model. The CsPO₃ crystal under investigation was twinned by mirroring at (100). Reflections of the individuals were separated and processed as HKL5 data. The refined ratio for the two twin domains was 0.7480(6):0.2520(6). Coordinates and atom numbering of CsPO₃ were adapted from the isotropic room-temperature modification of RbPO₃ [31].

Details of the data collections and structure refinements are gathered in Table 3. Further details of the crystal structure investigations may be obtained from The Cambridge Crystallographic Data Centre (CCDC) on quoting the depository numbers listed at the end of Table 3. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures.

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