ORIGINAL PAPER

The caesium phosphates $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$, $Cs_3(H_{1.5}PO_4)_2$, $Cs_4P_2O_7(H_2O)_4$, and $CsPO_3$

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Abstract

The caesium phosphates $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ and $Cs_3(H_{1.5}PO_4)_2$ were obtained from aqueous solutions, and $Cs_4P_2O_7(H_2O)_4$ and $CsPO_3$ from solid state reactions, respectively. $Cs_3(H_{1.5}PO_4)_2$, $Cs_4P_2O_7(H_2O)_4$, and $CsPO_3$ were fully structurally characterized for the first time on basis of single-crystal X-ray diffraction data recorded at -173 °C. Monoclinic $Cs_3(H_{1.5}PO_4)_2$ ($Z=2$, $C2/m$) 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 $Cs_4P_2O_7(H_2O)_4$ ($Z=2$, $P\bar{1}$) crystallizes also in a new structure type and is represented by a diphosphate 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. $CsPO_3$ is monoclinic ($Z=4$, $P2_1/n$) and belongs to the family of *catena*-polyphosphates $(MPO_3)_n$ with a repetition period of 2. It is isotypic with the room-temperature modification of $RbPO_3$. The crystal structure of $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ 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
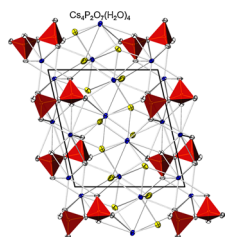
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Introduction

The recent interest in the family of caesium phosphates is mainly connected with the high proton conductivity of $Cs(H_2PO_4)$ 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 $M_xH_y(AO_4)_z$ ($M=$ Cs, Rb, K, Na, Li, NH_4; $A=$ S, Se, As, P) that likewise exhibit proton conductivity or have ferroelectric properties.

In this context, the new proton conductor $Cs_3(H_2PO_4)$-$(HPO_4)\cdot2H_2O$ ($= Cs_3(H_{1.5}PO_4)_2(H_2O)_2$) has been characterized lately [5].

Numerous caesium phosphates have been completely structurally characterized so far, viz. the low-temperature form of $Cs_3(PO_4)$ [6], $Cs_2(HPO_4)(H_2O)_2$ [7], $Cs(H_2PO_4)$ in its low- and room-temperature forms [8–10], as a super-protonic conductor phase [11] and in its high-pressure forms [12], $CsH_5(PO_4)_2$ [13], $Cs(H_3P_2O_7)(H_2O)$ [14], $Cs_2(H_2P_2O_7)$ [15], $Cs_6(P_6O_{18})(H_2O)_6$ [16], $Cs_3(P_3O_9)(H_2O)$ [17], $Cs_4(P_4O_{12})(H_2O)_4$ [18], and $Cs_8(P_8O_{24})(H_2O)_8$ [19].

Here, we report on the crystal structure refinements of the four caesium phosphates $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$, $Cs_3(H_{1.5}PO_4)_2$, $Cs_4P_2O_7(H_2O)_4$, 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 $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ [5] was re-evaluated, and the hydrous diphosphate $Cs_4P_2O_7(H_2O)_4$ 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[1] and P atoms in all structures very close to the expected formal total valencies of $+\mathrm{I}$ and $+\mathrm{V}$, respectively, with the highest deviation being 0.15 valence units for some P atoms (Table 1).

$Cs_3(H_{1.5}PO_4)_2(H_2O)_2$

Concerning the previous single-crystal X-ray study of $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ 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 $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ 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 ($O2\cdots O2(-x+1, -y, -z)$) 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 $Pbca$ (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 $O2–H\cdots O2'$ 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 $(NH_4)H_5(PO_4)_2$ [23], $Tl^IH_5(AsO_4)_2$ [24], or $Na_5H_3(SeO_4)_4(H_2O)_2$ [25].

Although the present low-temperature X-ray diffraction data for $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ clearly point to an unsymmetrical hydrogen bond $O2–H2\cdots O2(-x+1, -y, -z)$ 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 $O2\cdots O2'$ distance derived from the room-temperature measurement (2.445(7) Å [5]) is slightly longer than in the current low-temperature measurement (2.4343(19) 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 $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ 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 $160\,°C$ ($a = 11.1693(4)$, $b = 6.4682(2)$,

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

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

Cs1	OW	3.0975(15) 2x
Cs1	O4	3.1567(13) 2x
Cs1	O2	3.2124(13) 2x
Cs1	O1	3.4336(13) 2x
BVS		0.95
Cs2	O3	3.1241(15)
Cs2	OW	3.1384(15)
Cs2	O1	3.2209(13)
Cs2	OW	3.2475(15)
Cs2	O1	3.3836(12)
Cs2	O3	3.2626(13)
Cs2	O4	3.3093(13)
Cs2	O4	3.3492(13)
Cs2	O2	3.3898(14)
Cs2	O2	3.3909(13)
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

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

Cs1	O2	3.0836(17) 2x
Cs1	O1	3.2187(13) 4x
Cs1	O3	3.4031(13) 4x
BVS		1.07
Cs2	O3	3.0011(17)
Cs2	O2	3.1068(18)
Cs2	O1	3.1570(12) 2x
Cs2	O2	3.2709(12) 2x
Cs2	O1	3.2978(15) 2x
BVS		1.02
P1	O2	1.5030(15)
P1	O3	1.5459(15)
P1	O1	1.5697(9) 2x
BVS		4.85

Cs$_4$P$_2$O$_7$(H$_2$O)$_4$

Cs1	O5	3.0893(16)
Cs1	O1	3.1026(15)
Cs1	O1	3.1309(14)
Cs1	O5	3.1978(18)
Cs1	O3	3.2121(16)
Cs1	O4	3.2377(15)
Cs1	OW2	3.2581(18)
Cs1	O6	3.3426(17)
BVS		1.00
Cs2	O6	2.9595(16)
Cs2	O2	3.0542(17)
Cs2	O6	3.1487(15)
Cs2	OW3	3.2135(17)
Cs2	O3	3.2942(18)
Cs2	O2	3.3453(15)
Cs2	O4	3.3747(14)
Cs2	OW1	3.4432(18)
Cs2	O4	3.4619(15)
Cs2	O2	3.5818(14)
BVS		1.08
Cs3	OW3	3.0642(18)
Cs3	OW1	3.0754(18)
Cs3	OW3	3.2289(16)
Cs3	OW1	3.2819(19)
Cs3	OW2	3.2979(19)
Cs3	O2	3.2997(15)
Cs3	O6	3.3313(16)
Cs3	O7	3.3925(14)
Cs3	OW1	3.462(2)
BVS		0.95
Cs4	OW2	3.1116(14)
Cs4	O5	3.1304(13)
Cs4	OW2	3.1375(16)
Cs4	O7	3.2037(15)
Cs4	OW4	3.230(2)
Cs4	OW4	3.243(2)
Cs4	OW3	3.2576(17)
Cs4	O1	3.4014(16)
Cs4	OW4	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)

CsPO$_3$

Cs1	O3	3.0282(15)
Cs1	O2	3.0432(15)
Cs1	O2	3.0981(17)
Cs1	O3	3.0982(15)
Cs1	O3	3.1097(18)
Cs1	O2	3.1455(15)
Cs1	O1	3.3649(14)
BVS		1.06
P1	O2	1.4793(16)
P1	O3	1.4919(16)
P1	O1	1.6134(16)
P1	O1	1.6183(16)
BVS		4.87
P1 O1 P1		130.63(9)

Table 1 (continued)

Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$	Cs$_3$(H$_{1.5}$PO$_4$)$_2$	Cs$_4$P$_2$O$_7$(H$_2$O)$_4$			CsPO$_3$
		P2	O6	1.5214(16)	
		P2	O4	1.6350(13)	
		BVS		4.90	
		P1 O4 P2		128.49(10)	

Table 2 Details of hydrogen bonding/Å, °

D—H	A	d(D—H)	d(H···A)	d(D···A)	∠(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)
Ow Hw2	O3	0.85(3)	1.87(3)	2.706(2)	167(3)
O1 H1	O4	0.85(2)	1.72(3)	2.5444(18)	164(3)
O2 H2	O2	0.85(9)	1.60(9)	2.4343(19)	166(10)
Cs$_3$(H$_{1.5}$PO$_4$)$_2$					
O1 H1	O1	0.89(3)	1.71(2)	2.5513(16)	156(4)
O3 H3	O3	1.2288(16)	1.2288(16)	2.458(2)	180
Cs$_4$P$_2$O$_7$(H$_2$O)$_4$ [a]					
OW1	O2			2.725	
OW1	O7			2.744	
OW2	O6			2.682	
OW2	O7			2.713	
OW3	O1			2.701	
OW3	O3			2.721	
OW4	O3			2.724	
OW4	O5			2.760	

[a] All distances < 3.2 Å were considered

$c = 7.7442(3)$ 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 $C2$ (No. 5), whereas the current refinement clearly indicates the higher $C2/m$ 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 $2a$ (site symmetry $2/m$), Cs2, P1, O1, O2, O3 are all situated on position $4i$ (m), H1 ($8j$; 1) is disordered about a twofold rotation axis, and H3 is situated on Wyckoff position $2b$ ($2/m$).

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.

The caesium phosphates Cs₃(H₁.₅PO₄)₂(H₂O)₂, Cs₃(H₁.₅PO₄)₂,...

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Fig. 1 The hydrogen-bonding network (green and yellow lines) of $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ in a projection along [010] involving the hydrogen phosphate tetrahedra and water molecules. Displacement ellipsoids are drawn at the 90% probability level; phosphate tetrahedra are red, O atoms are white, O atoms of OH groups are green, water O atoms are yellow, and H atoms are given as grey spheres of arbitrary radius (colour figure online)
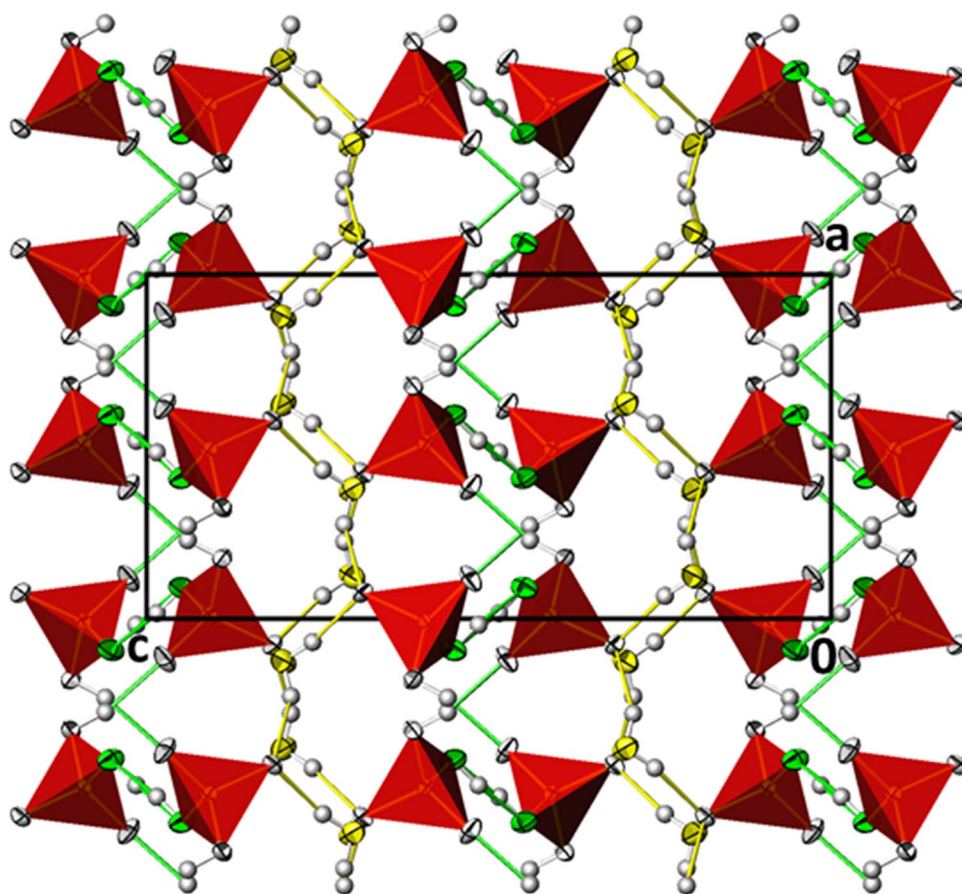
The two caesium cations are situated between the hydrogen-bonded chains (Fig. 6). Each Cs1 symmetrically links four chains; it exhibits a coordination number of 10 in form of a distorted hexadecahedron [26]. Cs1 is bonded to two (non-H atom bearing) O3 atoms of two neighbouring chains with the shortest 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).

$Cs_4P_2O_7(H_2O)_4$

In the crystal structure of $Cs_4P_2O_7(H_2O)_4$ (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. $Na_4P_2O_7(H_2O)_{10}$ [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 $K_4P_2O_7(H_2O)_3$ [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 $Cs_4P_2O_7(H_2O)_4$ 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 $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ in a projection along [100]. Displacement ellipsoids and colour codes are as in Fig. 1; Cs1 is given in dark blue, Cs2 in turquoise
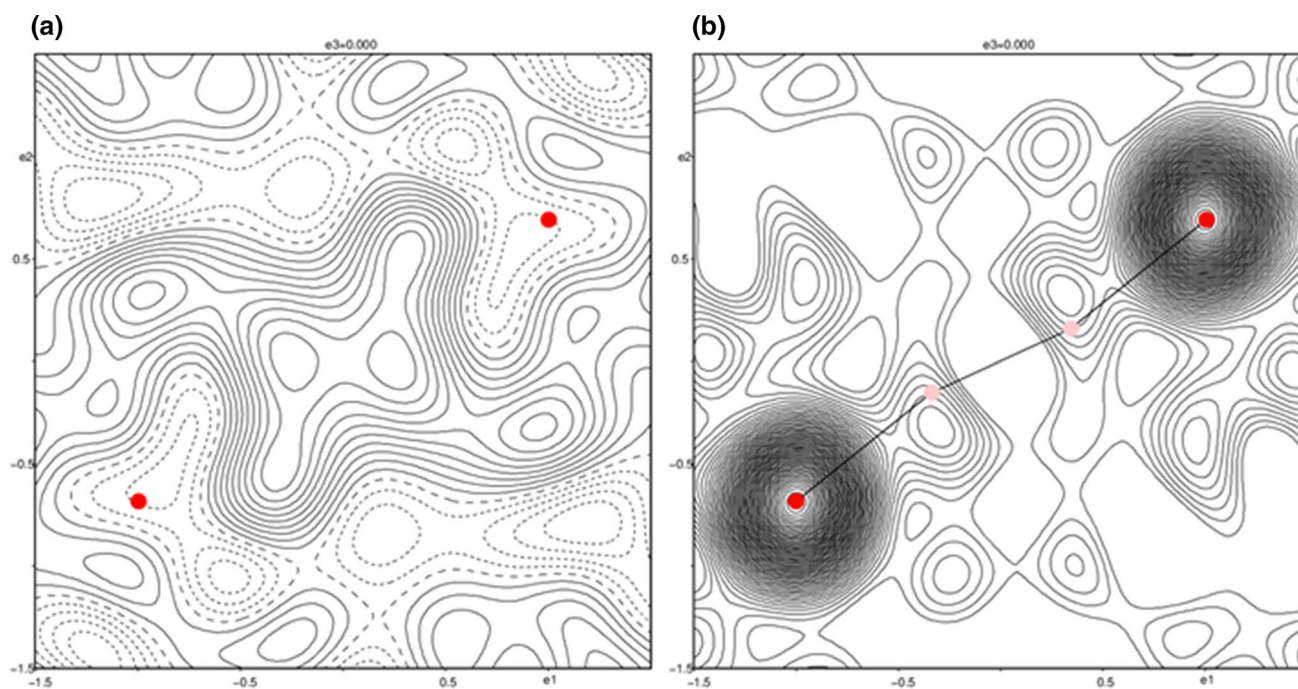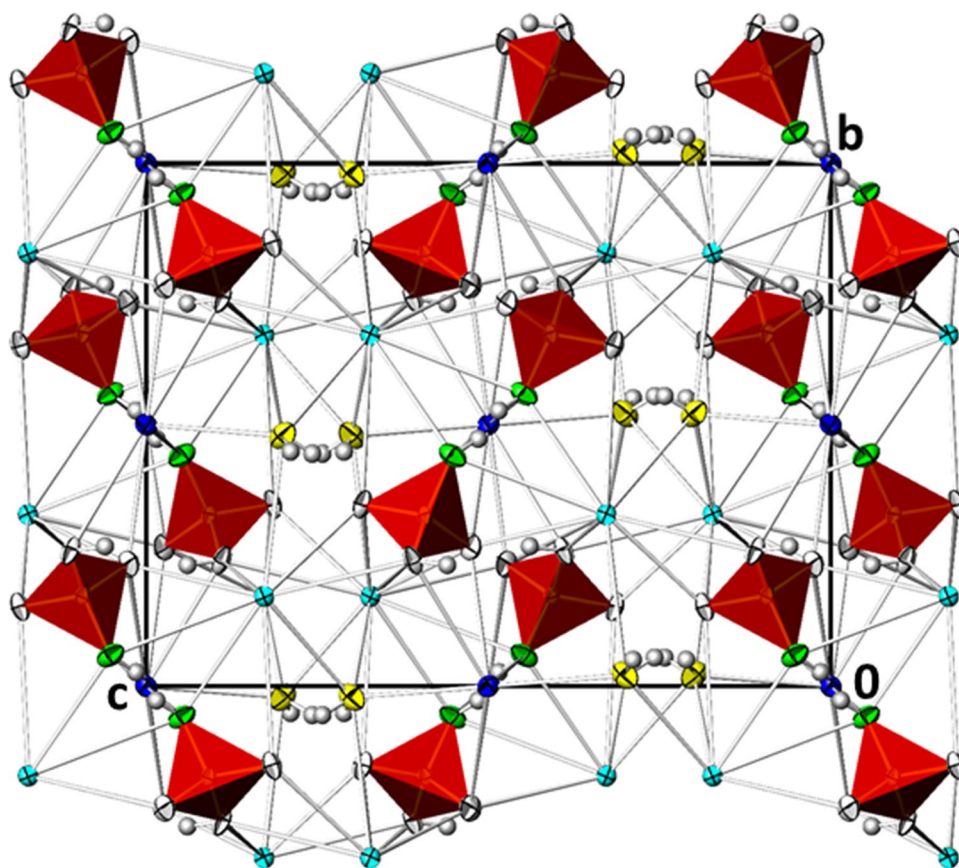

(a)

(b)

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_{obs} map with H atoms (pale pink dots). The sections are centred on the inversion centre at (½, 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)

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

Compound	$Cs_3(H_{1.5}PO_4)_2(H_2O)_2$	$Cs_3(H_{1.5}PO_4)_2$	$Cs_4P_2O_7(H_2O)_4$	$CsPO_3$
Diffractometer	—Bruker APEX2—			
Radiation; λ/Å	—MoK_a; 0.71073—			
Temperature/ °C	— −173—			
Crystal dimensions/mm^3	$0.09 \times 0.04 \times 0.01$	$0.15 \times 0.11 \times 0.02$	$0.32 \times 0.12 \times 0.02$	$0.05 \times 0.03 \times 0.01$
Crystal description	colourless plate	colourless plate	colourless plate	colourless fragment
Space group	$Pbca$	$C2/m$	$P\bar{1}$	$P2_1/n$
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)
α/°	90	90	77.2551(16)	90
β/°	90	108.578(3)	89.1014(17)	96.068(5)
γ/°	90	90	74.1314(16)	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
μ/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 θ_{min}–θ_{max}/°	2.76–35.12	2.79–40.36	1.90–35.05	3.25–32.61
Range				
$\quad h$	$-11 \rightarrow 11$	$-16 \rightarrow 20$	$-10 \rightarrow 10$	$-19 \rightarrow 19$
$\quad k$	$-17 \rightarrow 18$	$-11 \rightarrow 11$	$-16 \rightarrow 16$	$-6 \rightarrow 6$
$\quad l$	$-23 \rightarrow 22$	$-14 \rightarrow 14$	$-17 \rightarrow 17$	$-10 \rightarrow 10$
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_{min}; T_{max}	0.65; 0.91	0.13; 0.58	0.24; 0.81	0.005; 0.008
Ext. coef. [40]	1140(80)	230(19)	560(40)	–
Number of parameters	86	43	155	47
Δe_{max}; Δe_{min}/e$^-$ Å^{-3}	0.53; −0.50	0.91; −0.87	1.47; −0.78	0.99; −1.32
$R[F > 3\sigma(F)]$; $wR2(F$ 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

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.

$CsPO_3$

Corbridge reported crystallographic data of $CsPO_3$ and other alkali long-chain polyphosphates of formula $(MPO_3)_n$[2] (M = Na, K, Rb, Cs), showing that the Rb and

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[2] 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 PO_4 tetrahedron that are shared with a neighbouring 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 $(MPO_3)_n$ compounds. Hence, these compounds are also referred to as *catena*-metaphosphates.

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
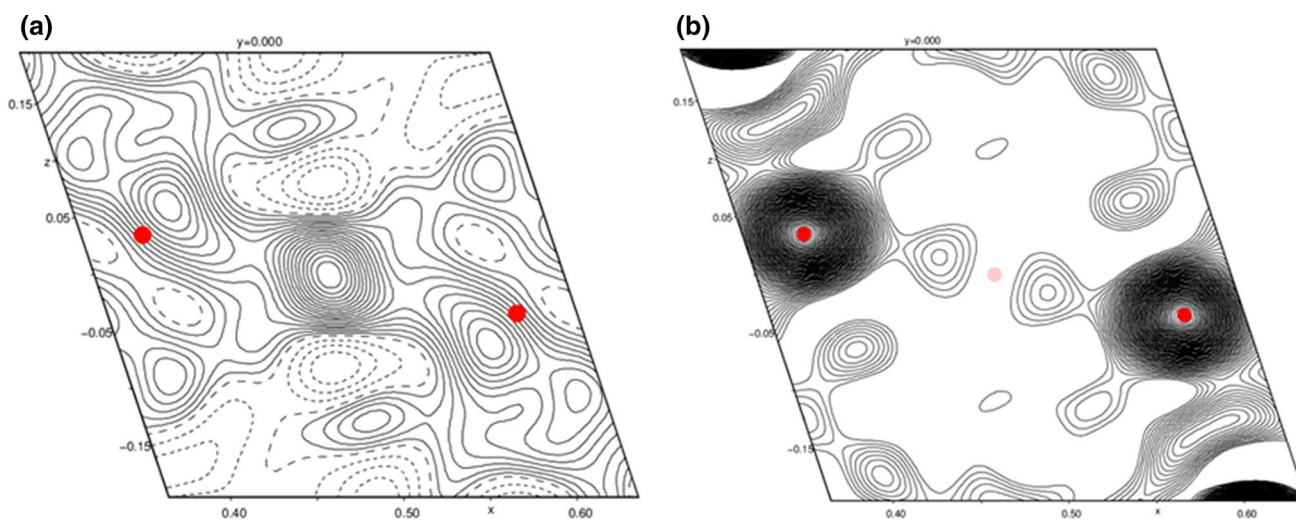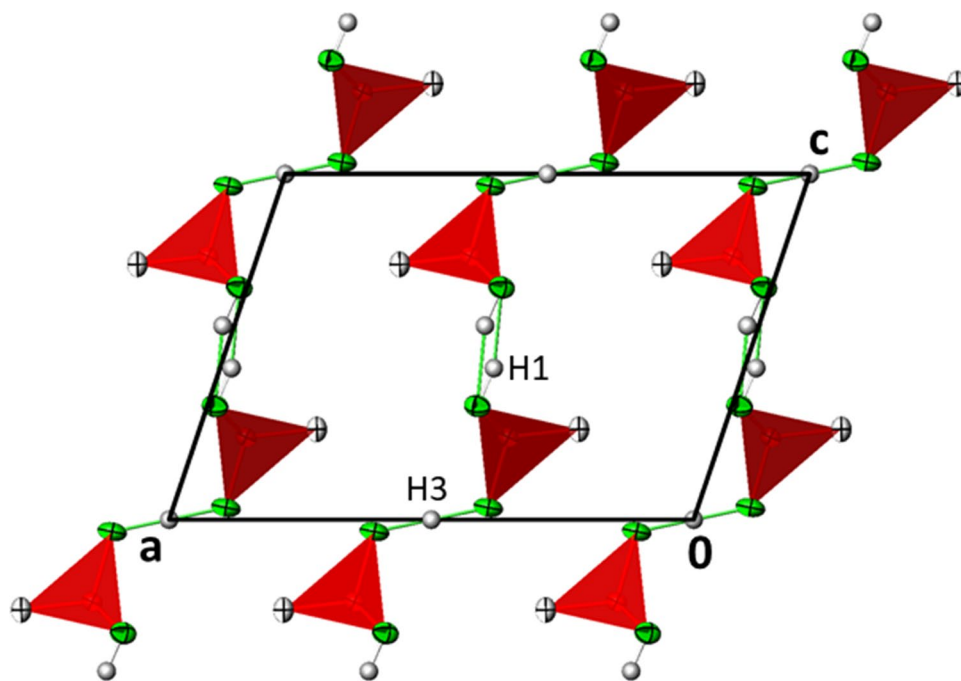

Fig. 5 a Difference Fourier map around symmetry-related O3 atoms (red points) on basis of a model with omission of the respective H atoms, showing one maximum situated at the 2/m position related to electron density of an ordered H atom; **b** F_{obs} map with H atom (pale pink dot). The plots represent $y = 0$ sections centred around (½, 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⁻/Å³ and **b** 0.5 e⁻/Å³ (colour figure online)

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, $\beta = 83°$ [20]) are in good agreement with the current low-temperature data (Table 3, with $\beta > 90°$ according to convention). Next to $CsPO_3$, $TlPO_3$ 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 (O2, O3) and two considerably longer P-O distances (average 1.616 Å) to bridging O atoms (O1 and O1(−x+1/2,

Fig. 6 The crystal structure of $Cs_3(H_{1.5}PO_4)_2$ in a projection along [001]. Displacement ellipsoids and colour codes are as in Fig. 2
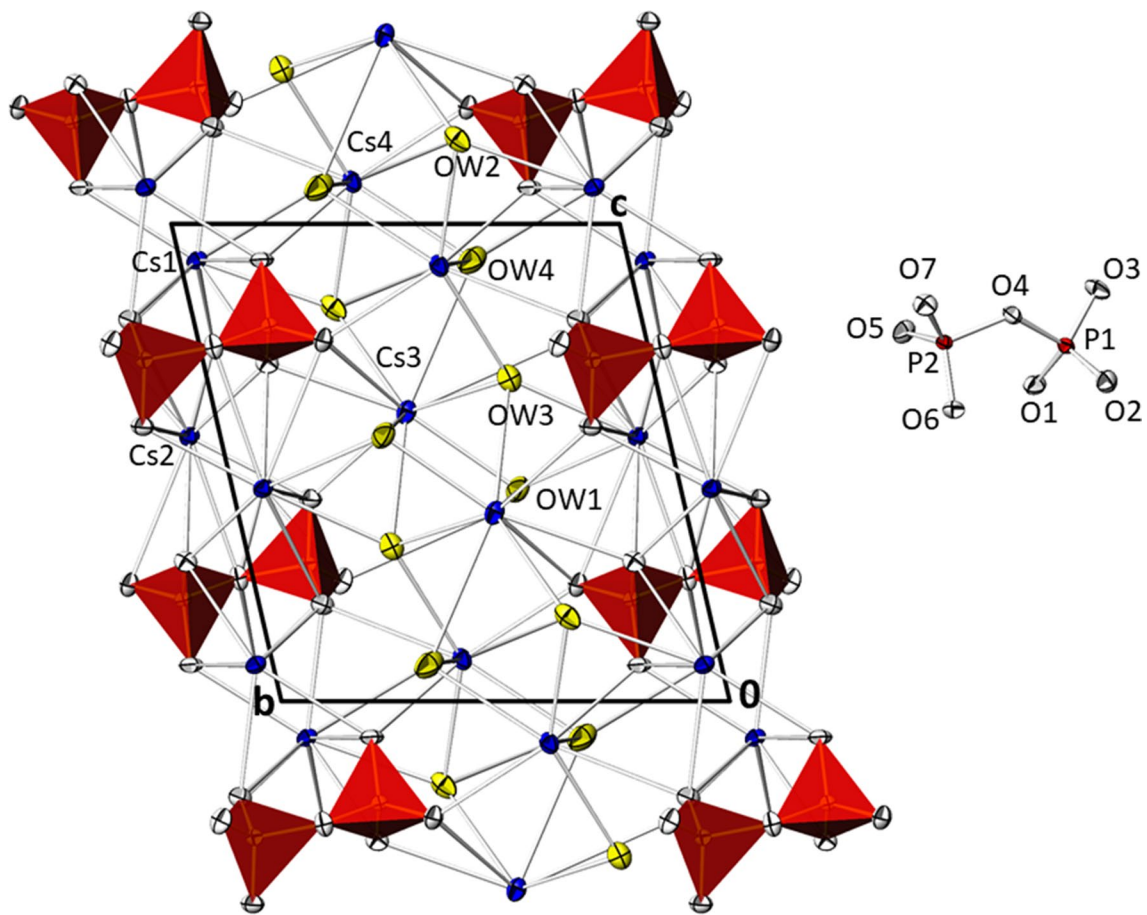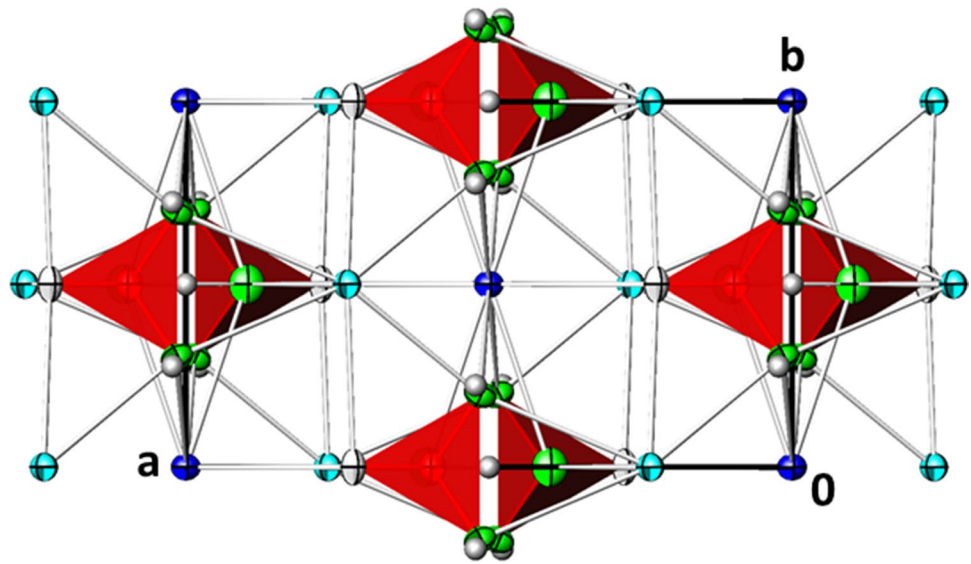

Fig. 7 The crystal structure of $Cs_4P_2O_7(H_2O)_4$ in a projection along [100]. Displacement ellipsoids and colour codes are as in Fig. 2. The inset shows the diphosphate group with atom labelling

Fig. 8 The crystal structure of CsPO$_3$ in a projection along [010]. Displacement ellipsoids and colour codes are as in Fig. 1. The inset shows the polyphosphate chains with a repetition period of 2 extending parallel [010]
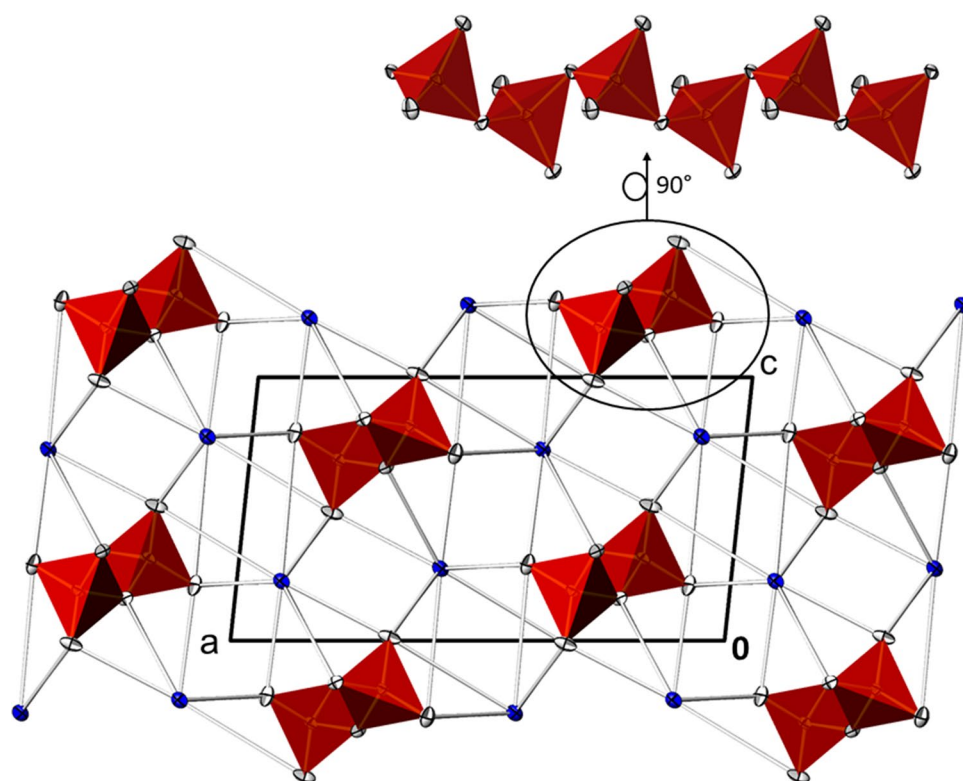
$y - 1/2$, $-z + 1/2$)). The Cs cations are situated in-between the chains and exhibit a coordination number of 7 with a monocapped prism as coordination polyhedron; Cs—O distances range from 3.03 to 3.37 Å (Table 1).

The program *compstru* [33], available at the Bilbao Crystallographic Server [34], was employed for a quantitative structural comparison of the isotypic CsPO$_3$ and RbPO$_3$ structures. For that purpose, the current low-temperature structure data of CsPO$_3$ and the room-temperature structure data of RbPO$_3$ 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 Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$, Cs$_3$(H$_{1.5}$PO$_4$)$_2$, Cs$_4$P$_2$O$_7$(H$_2$O)$_4$, and CsPO$_3$ were refined from low-temperature X-ray diffraction data at -173 °C. Although for the two hydrogen phosphates Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ and Cs$_3$(H$_{1.5}$PO$_4$)$_2$ 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 Cs$_4$P$_2$O$_7$(H$_2$O)$_4$, 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 Cs$_3$(H$_{1.5}$PO$_4$)$_2$ were isolated from a batch intended to produce Cs$_2$(HPO$_4$). To diluted phosphoric acid ($\approx 5\%_{wt}$), an aqueous solution of Cs$_2$CO$_3$ 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 Cs$_2$(HPO$_4$). After longer contact with ambient humidity at room temperature (about 2 days), crystals of the hydrate phase Cs$_3$(H$_{1.5}$PO$_4$)$_2$(H$_2$O)$_2$ were subsequently isolated from the original reaction product.

Crystals of $Cs_4P_2O_7(H_2O)_4$ were isolated from a batch intended to produce anhydrous $Cs_4P_2O_7$ from solid state reactions. $Cs_4P_2O_7$ was described as an intermediate product during thermal treatment of $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ [5] or $Cs_2(HPO_4)_2(H_2O)_2$ and was reported to be polymorphic [35]. Cs_2CO_3 and $(NH_4)_2HPO_4$ 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.

$CsPO_3$ was prepared by mixing a diluted solution of phosphoric acid ($\approx 5\%_{wt}$) and an aqueous solution of Cs_2CO_3 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 $Cs_3(H_{1.5}PO_4)_2$ and $Cs_3(H_{1.5}PO_4)_2(H_2O)_2$ 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 $Cs_3(H_{1.5}PO_4)_2$ where the H atom is located on Wyckoff position 2*b* (2/*m*). H atoms of the water molecules could not be localized reliably for $Cs_4P_2O_7(H_2O)_4$ and therefore are not included in the final crystal structure model. The $CsPO_3$ crystal under investigation was twinned by mirroring at (100). Reflections of the individuals were separated and processed as HKLF5 data. The refined ratio for the two twin domains was 0.7480(6):0.2520(6). Coordinates and atom numbering of $CsPO_3$ were adapted from the isotypic room-temperature modification of $RbPO_3$ [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.

References

1. Paschos O, Kunze J, Stimming U, Maglia F (2011) J Phys Condens Matter 23:234110
2. Haile SM, Chisholm CRI, Sasaki K, Boysen DA, Uda T (2007) Faraday Discuss 134:17
3. Kim G, Griffin JM, Blanc F, Haile SM, Grey CP (2015) J Am Chem Soc 137:3867
4. Nikiforov AV, Berg RW, Bjerrum NJ (2018) Ionics 24:2761
5. Ponomareva V, Bagryantseva I, Zakharov B, Bulina N, Lavrova G, Boldyreva E (2017) Acta Crystallogr C 73:773
6. Voronin VI, Berger IF, Proskurnina NV, Sheptyakov DV, Goshchitskii BN, Burmakin EI, Stroev SS, Shekhtman GS (2008) Neorg Mater 44:740
7. Stöger B, Weil M (2014) Acta Crystallogr C 70:7
8. Iwata Y, Koyano N, Shibuya I (1980) J Phys Soc Jpn 49:304
9. Ueso Y, Kobayashi J (1976) Phys Status Solidi A 34:475
10. Preisinger A, Mereiter K, Bronowska W (1994) Mater Sci Forum 166:511
11. Yamada K, Sagara T, Yamane Y, Ohki H, Okuda T (2004) Solid State Ion 175:557
12. Schuele PJ, Thomas R (1985) Jpn J Appl Phys 24:935
13. Efremov VA, Trunov VK, Matsichek I, Gudinitsa EN, Fakeev AA (1981) Zh Neorg Khim 26:3213
14. Larbot A, Durand J, Norbert A (1980) Rev Chim Mineral 17:5548
15. Averbuch-Pouchot MT, Durif A (1993) C R Acad Sci Ser II 316:41
16. Averbuch-Pouchot MT, Durif A (1989) C R Acad Sci Ser II 308:1699
17. Tordjman I, Masse R, Guitel JC (1977) Acta Crystallogr B 33:585
18. Averbuch-Pouchot MT, Durif A (1986) Acta Crystallogr C 42:131
19. Brühne B, Jansen M (1993) Z Anorg Allg Chem 619:1633
20. Corbridge DEC (1955) Acta Crystallogr 8:520
21. Brese NE, O'Keeffe M (1991) Acta Crystallogr B 47:192
22. Brown ID (2002) The chemical bond in inorganic chemistry: the bond valence model. Oxford University Press, Oxford
23. Troyanov SI, Snigireva EM, Kemnitz E (2000) Z Kristallogr 215:364
24. Schroffenegger M, Eder F, Weil M, Stöger B, Schwendtner K, Kolitsch U (2019) J Alloys Compd 820:153369
25. Pollitt S, Weil M (2014) Z Anorg Allg Chem 640:1622
26. Ruiz-Martínez A, Alvarez S (2009) Chem Eur J 15:7470
27. Durif A (1995) Crystal chemistry of condensed phosphates. Plenum Press, New York
28. McDonald WS, Cruickshank DWJ (1967) Acta Crystallogr 22:43
29. Corbridge DEC (1956) Acta Crystallogr 9:308
30. Cruickshank DWJ (1964) Acta Crystallogr 17:681
31. Holst C, Schmahl WW, Fuess H (1994) Z Kristallogr 209:322
32. El Horr N (1991) J Solid State Chem 90:386
33. de la Flor G, Orobengoa D, Tasci E, Perez-Mato JM, Aroyo MI (2016) J Appl Cryst 49:653

34. Aroyo MI, Perez-Mato JM, Capillas C, Kroumova E, Ivantchev S, Madariaga G, Kirov A, Wondratschek H (2006) Z Kristallogr 221:15

35. Lavrova GV, Bulina NV, Min'kov VS, Matvienko AA (2016) Russ J Inorg Chem 61:284

36. Apex-2 and Saint (2012) Bruker AXS Inc, Madison, Wisconsin

37. Krause L, Herbst-Irmer R, Sheldrick GM, Stalke D (2015) J Appl Crystallogr 48:3

38. Palatinus L, Chapuis G (2007) J Appl Crystallogr 40:786

39. Petříček V, Dušek M, Palatinus L (2014) Z Kristallogr 229:345

40. Becker PJ, Coppens P (1974) Acta Crystallogr A 30:129