

## A tetragonal polymorph of caesium hydroxide monohydrate, CsOH·H<sub>2</sub>O, from X-ray powder data

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Tetragonal caesium hydroxide monohydrate, CsOH·H<sub>2</sub>O, a clathrate hydrate, is a polymorph of three known hexagonal or pseudo-hexagonal modifications. It was obtained as a by-product in a high-pressure experiment. Whether it is a high-pressure polymorph, however, remains to be verified. The Cs atoms are situated in cavities of the form of a bicapped pentagonal prism, within an infinite three-dimensional hydrogen-bonded oxygen framework that is locally identical to layers found in the hexagonal modifications. The Cs atom and one of the two H atoms are at sites with  $\bar{4}m2$  symmetry, the O atom has  $mm$  site symmetry and the second H atom has  $2/m$  symmetry.

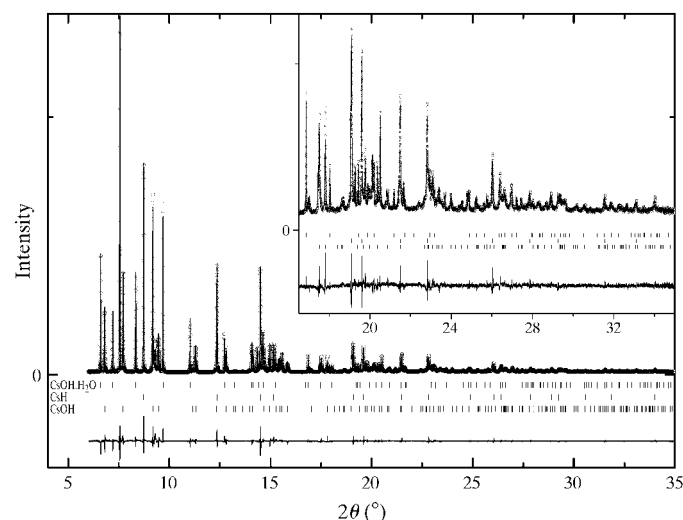
### Comment

Caesium hydroxide monohydrate, CsOH·H<sub>2</sub>O (or CsH<sub>3</sub>O<sub>2</sub>), is known to crystallize in three different hexagonal or pseudo-hexagonal modifications (Jacobs *et al.*, 1982). Below 233 K the symmetry is monoclinic, between 233 and 340 K it is trigonal, and above 340 K the structure becomes truly hexagonal, at least so far as the positions of the Cs and O atoms are concerned (space group  $P6/mmm$ ,  $a = 4.574$  and  $c = 4.440$  Å, Cs at  $1a$  and O at  $2d$ ). The O atoms form (001) layers with hexagonal symmetry, each O atom being connected to three neighbouring O atoms *via* hydrogen bonds. It has been shown by incoherent neutron scattering (Stahn *et al.*, 1983) that at 402 K the H atoms are dynamically disordered in a double-well potential between adjacent O atoms, indicating that at this temperature it is impossible to distinguish between OH<sup>-</sup> ions and water molecules, and the structure can thus be rationalized in terms of (001) two-dimensional H<sub>3</sub>O<sub>2</sub><sup>-</sup> ions separated by (001) layers of Cs<sup>+</sup> ions.

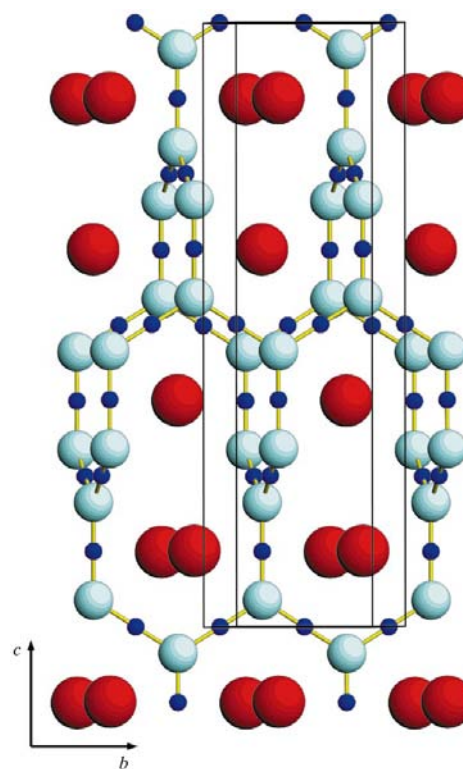
The Rietveld refinement of the synchrotron data (Fig. 1) measured on the present tetragonal polymorph shows that the

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same triangular coordination of O atoms as in the hexagonal polymorph can be found locally in the tetragonal phase, as bands running along the  $a$  axis at  $z \sim \frac{1}{4}$  and  $\frac{3}{4}$ , and along the  $b$  axis at  $z \sim 0$  and  $\frac{1}{2}$  (Fig. 2). These bands form an infinite three-



**Figure 1**  
Observed (circles) and calculated (solid line) intensities for CsOH·H<sub>2</sub>O. The three rows of tick-marks indicate, from top to bottom, the positions of the Bragg peaks of the main (CsOH·H<sub>2</sub>O) and impurity (CsH and CsOH) phases. The difference pattern appears below.



**Figure 2**  
The structure of CsOH·H<sub>2</sub>O viewed approximately along the  $a$  axis. The positions of the H atoms (small spheres) were predicted from bond-valence analysis. Cs atoms are denoted by large spheres and O atoms by mid-sized spheres.

dimensional oxygen framework that is locally identical to the layers found in the hexagonal modification.

No H atoms were identified during the refinement, so the concept of bond valences (Brown & Wu, 1976) was used to locate the hydrogen bonds. The data of Brese & O'Keeffe (1991) were used to calculate the bond valences for all non-H atoms. The bond valences sum to 0.94 for Cs and to 0.47 for O, indicating that each O atom participates in three hydrogen bonds. Neutron diffraction on a deuterated sample would be necessary to localize the H atoms precisely and to determine whether, at room temperature, they are fully ordered (which would lead to a decrease of the symmetry) or disordered, as in the hexagonal polymorph.

The Cs atoms are situated in the cavities of the oxygen framework, taking the form of a bicapped pentagonal prism. This form can be derived from a hexagonal prism (the Cs coordination observed in the hexagonal modification) by a 90° rotation of half of the hexagonal prism.

The tetragonal polymorph of CsOH·H<sub>2</sub>O is a clathrate hydrate. The calculated density of the tetragonal modification of CsOH·H<sub>2</sub>O at ambient pressure and 293 K is 3.79 Mg m<sup>-3</sup>, which is higher than the density of the hexagonal polymorph, which was found to be 3.51 Mg m<sup>-3</sup> at the same temperature and pressure.

## Experimental

The tetragonal modification of CsOH·H<sub>2</sub>O was initially obtained as a by-product during the high-pressure synthesis of caesium-based ternary metal hydrides. In the first step, binary caesium hydride powder was synthesized by direct hydrogenation of a metallic caesium ingot (STREM, 99.9%) at 700 K and 80 bar (1 bar = 10<sup>5</sup> Pa) hydrogen pressure for 15 d in an autoclave. In the second step, caesium-based metal hydrides were synthesized by heating mixtures of CsH and the corresponding metal to 800 K in a multi-anvil press at 30 kbar pressure in air. The reaction products contained CsOH and tetragonal CsOH·H<sub>2</sub>O as impurities. The same experiments were performed without the metal powders, and the reaction product contained CsH, CsOH and tetragonal CsOH·H<sub>2</sub>O. The product was white, pyrophoric and extremely sensitive to air and moisture.

### Crystal data

CsOH·H <sub>2</sub> O	Cell parameters from 109 reflections
$M_r = 167.93$	$\theta = 3.3\text{--}25^\circ$
Tetragonal, $I4_1/amd$	$\mu = 24.21 \text{ mm}^{-1}$
$a = 4.38088 (4) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.46525 (17) \text{ \AA}$	Specimen shape: cylinder
$V = 296.811 (5) \text{ \AA}^3$	$50 \times 0.4 \times 0.4 \text{ mm}$
$Z = 4$	Specimen prepared at 3 000 000 kPa
$D_x = 3.785 (2) \text{ Mg m}^{-3}$	Specimen prepared at 800 K
Synchrotron radiation	Particle morphology: plate-like,
$\lambda = 0.48562 \text{ \AA}$	white

**Table 1**

Selected interatomic distances (Å).

Cs—O <sup>i</sup>	3.341 (3)	O—O <sup>ii</sup>	2.505 (11)
Cs—O <sup>ii</sup>	3.410 (6)	O—O <sup>iii</sup>	2.579 (6)

Symmetry codes: (i)  $\frac{1}{2} - x, y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{4} - y, \frac{1}{4} - x, \frac{3}{4} - z$ ; (iii)  $x, -y, 1 - z$ .

### Data collection

Two-axis goniometer diffractometer SNBL at the ESRF Grenoble, France	Specimen mounted in transmission mode
Specimen mounting: glass capillary	$2\theta_{\min} = 6.012, 2\theta_{\max} = 36.488^\circ$
	Increment in $2\theta = 0.002^\circ$

### Refinement

$R_p = 0.125$	Profile function: pseudo-Voigt
$R_{wp} = 0.133$	109 reflections
$R_{exp} = 0.059$	14 parameters
$S = 2.28$	H-atom parameters not refined
$2\theta_{\min} = 6.012, 2\theta_{\max} = 36.488^\circ$	$w = 1/Y_i$
Increment in $2\theta = 0.002^\circ$	$(\Delta/\sigma)_{\max} = 0.01$
Wavelength of incident radiation: 0.48562 Å	Preferred orientation correction: no

Data collection: SNBL data collection software; cell refinement: *FULLPROF98* (Rodríguez-Carvajal, 1998); data reduction: *FULLPROF98*; program(s) used to solve structure: *FOX* (Favre-Nicolin & Černý, 2001); program(s) used to refine structure: *FULLPROF98*; molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *WinPLOTR* (Roissnel & Rodríguez-Carvajal, 1998) and *ATOMS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1352). Services for accessing these data are described at the back of the journal.

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