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A new cubic form of caesium hexaaquamagnesium phosphate, $Cs[Mg(H_2O)_6](PO_4)$

Werner Massa,[a]* Olga V. Yakubovich[b] and Olga V. Dimitrova[b]

[a]Fachbereich Chemie, Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany, and [b]Department of Geology, Moscow Lomonosov State University, Vorob'evy Gory, 119899 Moscow, Russia
Correspondence e-mail: massa@chemie.uni-marburg.de

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A new cubic form (space group $F\bar{4}3m$) of the title compound has been found which is isostructural with the analogous arsenate. $[Mg(H_2O)_6]^{2+}$ cations and phosphate anions are connected by hydrogen bonds, forming a sphalerite-like three-dimensional framework.

Comment

In the course of investigations of magnesium phosphate minerals, such as bakchisaraitsevite $[Na_2(Mg_{4.5}Fe_{0.5})(PO_4)_4]\cdot 7H_2O$ (Yakubovich *et al.*, 2000), and their synthetic relatives, we have studied the products of soft hydrothermal syntheses in the Cs_3PO_4–$Mg(OH)_2$–H_2O system and found crystals of a new polymorph of $Cs[Mg(H_2O)_6](PO_4)$. Its structure has been determined by single-crystal X-ray diffraction and the results are presented here. A hexagonal form of this compound is already known (Ferrari *et al.*, 1955) and a cubic structure was deduced from powder diffraction data for the As analogue, $Cs[Mg(H_2O)_6](AsO_4)$.

The present crystal of $Cs[Mg(H_2O)_6](PO_4)$ belongs to the cubic $F\bar{4}3m$ space group. According to the high site symmetry ($\bar{4}3m$) of the 4*a* position, the Mg^{2+} ions occupy regular octahedra formed by the O2 atoms, with Mg—O distances of 2.065 (3) Å (Fig. 1 and Table 1). H atoms were localized and refined on the 48*h* position, resulting in a sensible geometry for the aqua ligands.

Regular PO_4 tetrahedra are connected 'face-to-face' to four neighbouring $[Mg(H_2O)_6]^{2+}$ cations by three strong hydrogen bonds [$O2\cdots O1 = 2.649$ (2) Å and $O2-H\cdots O1 = 173$ (5)°; Figs. 1 and 2, and Table 2]. Conversely, the octahedral cations are tetrahedrally surrounded by four anions. Thus, a sphalerite-like three-dimensional framework is formed, with $[Mg(H_2O)_6]^{2+}$ and PO_4^{3-} ions in the positions of the Zn^{2+} and S^{2-} ions, respectively. The Cs^+ cations lie on positions 4*d* alternating with the PO_4 positions on 4*c* (Fig. 2), and each Cs^+ cation is located at the centre of a cuboctahedron of 12 H_2O ligands belonging to four $[Mg(H_2O)_6]^{2+}$ cations. If the contacts of the Cs^+ anions to these ligands are included, the O2-atom environment is approximately trigonal pyramidal. The two cations and the phosphate anion form cubic *F*-centred sublattices with shifted origins in 0,0,0 (Mg), $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ (P) and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ (Cs), respectively. Thus, this simple cubic structure can also be derived from a rock-salt-type $[Cs(PO_4)]^{2-}$ structure, with $[Mg(H_2O)_6]^{2+}$ cations in every second centre of the $Cs_4(PO_4)_4$ subcubes. This structure corresponds to that proposed for the arsenate analogue, $Cs[Mg(H_2O)_6](AsO_4)$, on the basis of powder diffraction data (Ferrari *et al.*, 1955*a*,*b*). The atomic radius of As is larger than that of P, which is consistent with the unit-cell volume of the arsenate being ~6% larger than that of the phosphate. For the latter, Ferrari *et al.* (1955*a*,*b*) found a hexagonal form [space group $P6_3mc$; $a = 6.939$ (2) Å and $c = 11.896$ (2) Å]. The volume per formula unit in the cubic polymorph [252.3 (1) Å^3] is slightly larger (1.7%) than that in the hexagonal form (248.0 Å^3), which points to metastability of the cubic form.

The differences between the two structural forms can be described in terms of different sequences of close-packed layers of the Cs^+, $[Mg(H_2O)_6]^{2+}$ and PO_4^{3-} components.

In the cubic form, each sublattice is arranged along the [111] direction in a cubic close packing (ccp), as indicated in Fig. 3(*a*) by the *ABC* (PO_4), *bca* $[Mg(H_2O)_6]$ and $\gamma\alpha\beta$ (Cs) sequences. In addition, the sequence of these alternating layers is also of the ccp type ($Ab\gamma$ $Bc\alpha$ $Ca\beta$). In the hexagonal form, the $[Mg(H_2O)_6]^{2+}$ and Cs^+ cations form hexagonal close-packed sequences (*bcb* and $\gamma\beta\gamma$) along the *c* axis. The phosphate anions are aligned along *c*, but with an alternating orientation (*AA'A*; Fig. 3*b*).

A similar pseudo-hexagonal unit cell can be identified in the orthorhombic structures (space group $Pmn2_1$) of two analogues of the title compound, *viz*. the mineral struvite,

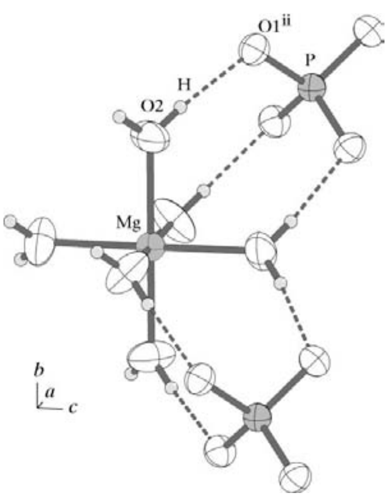

Figure 1
A *DIAMOND* (Brandenburg, 1999) drawing of the $[Mg(H_2O)_6]^{2+}$ cation and two neighbouring phosphate anions, with the atomic numbering scheme. Displacement ellipsoids have been drawn at the 50% probability level and hydrogen bonds are shown as dashed lines. [Symmetry code: (iii) $x, \frac{1}{2}-y, \frac{1}{2}-z$.]

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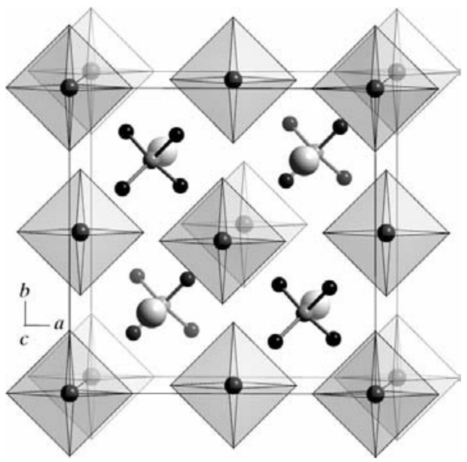

Figure 2
A view of the unit cell of $Cs[Mg(H_2O)_6](PO_4)$. Octahedra, tetrahedra and spheres represent $[Mg(H_2O)_6]^{2+}$ cations, PO_4^{3-} anions and Cs^+ cations, respectively.

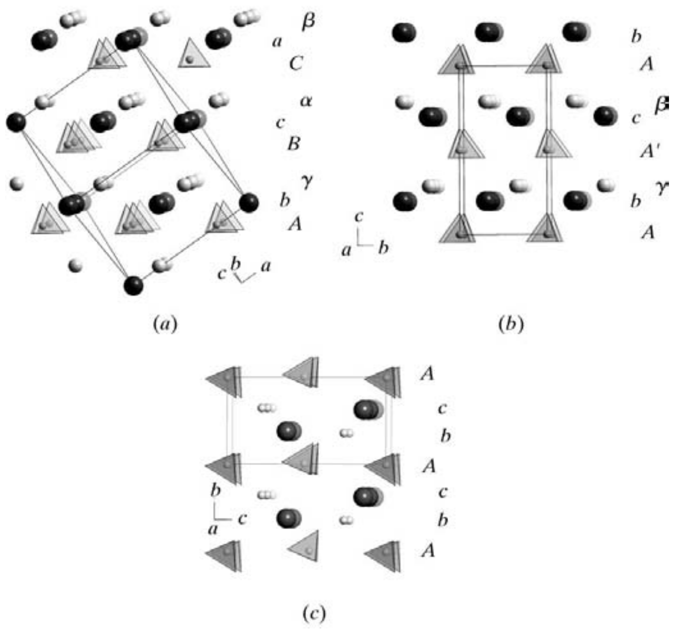

Figure 3
A comparison of the stacking layers in (*a*) cubic $Cs[Mg(H_2O)_6](PO_4)$, (*b*) hexagonal $Cs[Mg(H_2O)_6](PO_4)$ and (*c*) struvite, *viz.* $NH_4[Mg(H_2O)_6]$-(PO_4). Large spheres represent $[Mg(H_2O)_6]^{2+}$ cations, small spheres represent Cs^+ or NH_4^+ cations, and tetrahedra represent PO_4^{3-} anions.

$(NH_4)Mg(H_2O)_6(PO_4)$, which seems to form as a result of bacterial attack on organic material (Whitaker & Jefferey, 1970; Dickens & Brown, 1972; Abbona *et al.*, 1986; Ferraris *et al.*, 1986), and a synthetic phase, $KMg(H_2O)_6(PO_4)$ (Mathew & Schröder, 1979). According to Dickens & Brown (1972), the *h*0*l* reflections of struvite show pseudo-hexagonal symmetry. As shown in Fig. 3(*c*), layers of PO_4 tetrahedra are now stacked in a hexagonal primitive sequence (*AAA*). In contrast to the structure of the Cs compound, mixed layers of $[Mg(H_2O)_6]^{2+}$ and ammonium cations are interspersed with layers of the phosphate anions, resulting in a cubic sequence (*AbcAbc*).

The different packings in these related compounds correlate with significant differences in the hydrogen-bonding networks. In the cubic Cs compound, the $[Mg(H_2O)_6]^{2+}$ cations are tetrahedrally surrounded by four phosphate anions with four 'face-to-face' triple hydrogen bonds. Although no H-atom positions are reported for the hexagonal form, it can be concluded from the $O\cdots O$ distances that the $[Mg(H_2O)_6]^{2+}$ cations are surrounded by six PO_4 anions in a trigonal-prismatic arrangement and are connected by three 'edge-to-corner' and three 'corner-to-edge' hydrogen bonds. A similar trigonal prismatic coordination is found in the struvite structure, which is connected by two 'face-to-face', one 'edge-to-edge' and three 'corner-to-corner' hydrogen bonds. In addition, an $O-H\cdots N$ hydrogen bond links one of the aqua ligands to the ammonium cation.

Experimental

$Cs[Mg(H_2O)_6](PO_4)$ was formed by hydrothermal synthesis in the Cs_3PO_4–$Mg(OH)_2$–H_2O system [$T = 553$ K, $P = 7 \times 10^6$ Pa, $t = 20$ d, ratio $Cs_3PO_4/Mg(OH)_2 = 1:1$] in 7 ml Cu tubes in a steel autoclave. Very small (<0.05 mm) colourless octahedral crystals were formed, often in aggregates of 15–20 crystals. The presence of Cs, P and Mg atoms in the samples was confirmed by qualitative X-ray spectral analysis (CamScan 4DV and EDA Link AN 1000).

Crystal data

$Cs[Mg(H_2O)_6](PO_4)$
$M_r = 360.29$
Cubic, $F\bar{4}3m$
$a = 10.0308$ (14) Å
$V = 1009.3$ (2) Å^3
$Z = 4$
$D_x = 2.371$ Mg m^{-3}
Mo $K\alpha$ radiation

Cell parameters from 2068 reflections
$\theta = 3.5$–$29.6°$
$\mu = 3.92$ mm^{-1}
$T = 295$ (2) K
Octahedron, colourless
$0.04 \times 0.04 \times 0.04$ mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 1996)
$T_{min} = 0.774$, $T_{max} = 0.831$
1751 measured reflections

176 independent reflections
163 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 29.7°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 12$

Table 1
Selected geometric parameters (Å).

$Cs-O2^{i}$	3.5740 (6)	$P-O1$	1.539 (3)
$Mg-O2$	2.065 (3)		

Symmetry code: (i) $1-y, 1+z, 1-x$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H\cdots O1^{ii}$	0.82 (4)	1.83 (3)	2.649 (2)	173 (5)

Symmetry code: (ii) $x, \frac{1}{2}-y, \frac{1}{2}-z$.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.035$
$S = 1.11$
176 reflections
14 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983), 77 Friedel pairs
Flack parameter = −0.04 (3)

Data collection: *Win-Xpose* in *X-AREA* (Stoe & Cie, 2000); cell refinement: *Win-Cell* in *X-AREA*; data reduction: *Win-Integrate* in *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1018). Services for accessing these data are described at the back of the journal.

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