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A new hexagonal polymorph of magnesium perchlorate hexahydrate obtained from an acetamide medium

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A new magnesium perchlorate hexahydrate phase, $Mg(ClO_4)_2 \cdot 6H_2O$, was obtained from the mixed solvents of water and acetamide. The structure crystallizes in the hexagonal space group $P63mc$ and is isostructural with previously reported $M(ClO_4)_2 \cdot 6H_2O$ (M = Zn, Ni, Fe) phases. The Mg site is half occupied, indicating positional disorder of the metal cation. Prolonged crystallization leads to the formation of larger crystals consistent with an expanded unit cell, suggesting the formation of a disorder-related superstructure. The Mg, Cl and one of the O atoms have $3m.$ site symmetry.

1. Chemical context

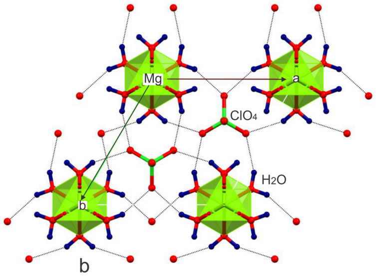
Magnesium perchlorate, $Mg(ClO_4)_2$, forms several hydrated crystalline phases, including the dihydrate, tetrahydrate and hexahydrate, which exhibit structural variability depending on crystallization conditions. Early studies described the hexahydrate as orthorhombic, while later investigations revealed additional structural complexity and possible disorder effects. Previously reported crystal structures of magnesium perchlorate hydrates include orthorhombic and monoclinic phases (West, 1934; Robertson & Bish, 2010; Solovyov, 2012).

Compounds of the general type $M(ClO_4)_2 \cdot 6H_2O$ (M = Zn, Ni, Fe) have been reported to adopt closely related structures characterized by metal-site disorder and partial occupancies (Ghosh & Ray, 1976; Ghosh *et al.*, 1997). These studies demonstrate that the disorder of the metal position is an intrinsic feature of this structural family and plays a key role in determining symmetry and phase behavior.

The present structure therefore represents a hexagonal polymorph of magnesium perchlorate hexahydrate, distinct from previously reported orthorhombic and monoclinic forms. The compound was obtained from an acetamide-containing medium, indicating that the crystallization environment plays a significant role in directing phase formation in the Mg–ClO_4–H_2O system.

2. Structural commentary

The title compound, $Mg(ClO_4)_2 \cdot 6H_2O$, crystallizes in the hexagonal space group $P63mc$ with $a = b = 7.7942$ (3) Å and $c = 5.2703$ (3) Å. The Mg^{2+} cation (site symmetry $3m.$) is coordinated by six water molecules, forming a slightly distorted octahedral $[Mg(H_2O)_6]^{2+}$ environment (Fig. 1). The six Mg—O distances are identical by symmetry at 2.126 (5), while the perchlorate anions retain their usual tetrahedral geometry with Cl—O distances of 1.426 (5) and 1.428 (3) Å.



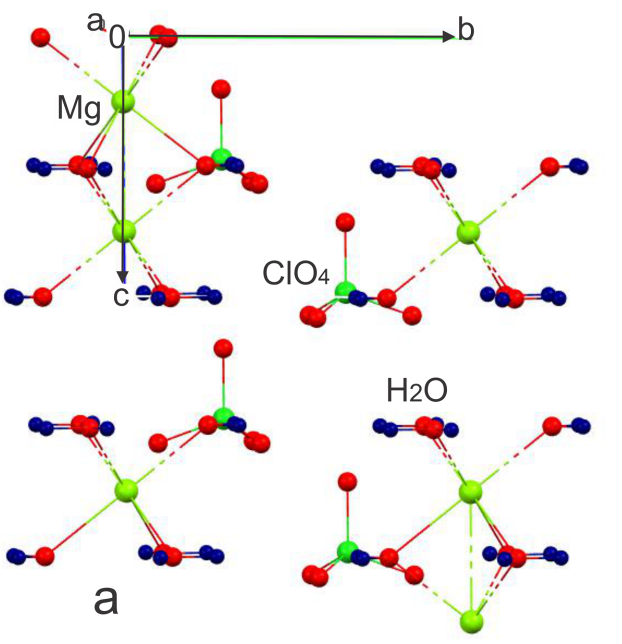


Figure 1
Arrangement of $Mg(H_2O)_6$ octahedra and ClO_4 tetrahedra in $Mg(ClO_4)_2·6H_2O$ viewed along [100]. Hydrogen bonds are shown as dashed lines.

The magnesium octahedra are connected through shared faces [Mg1···Mg1 = 2.63515 (15) Å], forming infinite chains extending along the [001] direction with Mg1—O1—Mg1 = 76.57 (9)°. The half-occupancy of the Mg site implies the presence of disordered interruptions within these chains, resulting in vacant positions along the columns. When this interruption becomes ordered, a lowering of symmetry occurs, leading to orthorhombic structures (Ghosh *et al.*, 1997). In contrast, when the disorder is maintained, the structure retains higher symmetry in the hexagonal space group. This behavior is consistent with previously reported Zn and Ni perchlorate hexahydrate structures (Ghosh & Ray, 1976), where similar disorder-driven symmetry relationships have been observed.

The perchlorate anions (Cl site symmetry $3m.$) occupy interstitial positions and consolidate the structure through electrostatic interactions. During crystallization, large needle-shaped crystals were observed, corresponding to an expanded unit cell of approximately 15 × 15 × 5 Å. This suggests the formation of a superstructure related to partial disorder or long-range ordering effects.

3. Supramolecular features

The structure is consolidated by O1—H1···O3^{i} [symmetry code: (i) $1 - x + y, 1 - x, z$) hydrogen bonds involving the coordinated water molecule [H···O = 2.20 Å, O···O = 3.041 (4) Å, O—H···O = 155°], which link the coordination octahedra into a three-dimensional network. The arrangement of the octahedral chains and hydrogen-bond network viewed along the [001] direction is shown in Fig. 2.

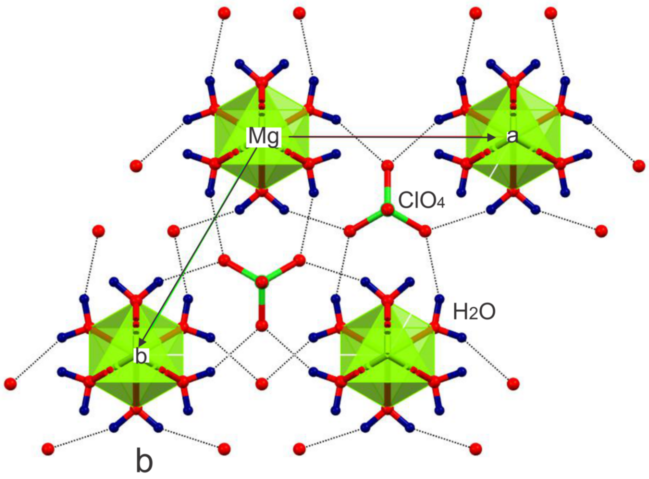


Figure 2
Packing of the crystal structure of $Mg(ClO_4)_2·6H_2O$ viewed along [001], illustrating the hydrogen-bonded framework and disordered octahedral chains.

4. Database survey

Previously reported crystal structures of magnesium perchlorate hydrates include orthorhombic and monoclinic polymorphs (West, 1934; Robertson & Bish, 2010; Solovyov, 2012). Related disordered perchlorate hexahydrates containing divalent metal cations such as Zn, Ni and Fe have also been described (Ghosh & Ray, 1976; Ghosh *et al.*, 1997). These compounds exhibit similar disorder-related structural features, including partial occupancies of the metal positions and disorder-driven symmetry relationships between hexagonal and orthorhombic forms.

5. Synthesis and crystallization

The compound was obtained in the system $Mg(ClO_4)_2$:*m*(acetamide):*n*(H_2O) by solution crystallization followed by slow evaporation at room temperature. The mixture forms a viscous liquid phase.

Crystallization occurs over approximately two days, yielding large needle-like crystals suitable for single-crystal X-ray diffraction at early stages. Continued crystallization leads to deterioration in crystal quality and increased structural disorder.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The model indicates the presence of disorder, as reflected in elevated displacement parameters and features identified in the *checkCIF* analysis. The hydrogen atom of the coordinated water molecules was included in a calculated position and refined using a riding model.

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Computing details

Magnesium perchlorate hexahydrate

Crystal data

$Mg(ClO_4)_2·6H_2O$
$M_r = 165.65$
Hexagonal, $P6_3mc$
$a = 7.7942$ (3) Å
$c = 5.2703$ (3) Å
$V = 277.27$ (3) Å^3
$Z = 2$
$F(000) = 170$
$D_x = 1.984$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4768 reflections
$\theta = 3.0–25.9°$
$\mu = 0.72$ mm^{-1}
$T = 273$ K
Block, clear white
0.2 × 0.1 × 0.1 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.870$, $T_{max} = 0.932$
7335 measured reflections
234 independent reflections
229 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.065$
$S = 1.20$
234 reflections
22 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.061P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Absolute structure: Flack x determined using 98 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.04 (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	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0.000000	0.000000	0.2498 (12)	0.0239 (7)	0.5
O1	0.12365 (19)	−0.12365 (19)	0.5000 (9)	0.0467 (7)	
H1	0.255441	−0.078800	0.499143	0.070*	
Cl1	0.666667	0.333333	0.49460 (13)	0.0291 (4)	
O2	0.666667	0.333333	0.2241 (10)	0.0576 (17)	
O3	0.8658 (5)	0.4329 (2)	0.5864 (8)	0.0579 (10)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0220 (9)	0.0220 (9)	0.0277 (12)	0.0110 (4)	0.000	0.000
O1	0.0418 (10)	0.0418 (10)	0.0639 (14)	0.0264 (11)	0.0007 (9)	−0.0007 (9)
Cl1	0.0237 (5)	0.0237 (5)	0.0400 (6)	0.0118 (2)	0.000	0.000
O2	0.067 (3)	0.067 (3)	0.040 (3)	0.0333 (13)	0.000	0.000
O3	0.0294 (16)	0.0534 (15)	0.083 (2)	0.0147 (8)	−0.0159 (15)	−0.0079 (8)

Geometric parameters (Å, º)

Mg1—Mg1^{i}	2.6352 (1)	Mg1—O1^{vi}	2.126 (5)
Mg1—Mg1^{ii}	2.6351 (1)	O1—H1	0.9046
Mg1—O1^{i}	2.126 (5)	O1—H1^{vii}	0.9046
Mg1—O1	2.127 (5)	Cl1—O2	1.426 (5)
Mg1—O1^{iii}	2.127 (5)	Cl1—O3	1.428 (3)
Mg1—O1^{iv}	2.126 (5)	Cl1—O3^{viii}	1.428 (3)
Mg1—O1^{v}	2.127 (5)	Cl1—O3^{ix}	1.428 (3)
O1^{i}—Mg1—O1^{v}	94.35 (6)	O1^{iv}—Mg1—O1^{iii}	94.35 (6)
O1^{vi}—Mg1—O1^{iii}	94.35 (6)	Mg1^{ii}—O1—Mg1	76.57 (9)
O1^{vi}—Mg1—O1^{i}	85.7 (2)	Mg1^{ii}—O1—H1^{vii}	120.83 (7)
O1^{i}—Mg1—O1	94.35 (6)	Mg1^{ii}—O1—H1	120.8
O1^{iv}—Mg1—O1	94.35 (6)	Mg1—O1—H1^{vii}	120.39 (7)
O1^{vi}—Mg1—O1^{v}	94.35 (6)	Mg1—O1—H1	120.4
O1^{iv}—Mg1—O1^{i}	85.7 (2)	H1—O1—H1^{vii}	99.1
O1—Mg1—O1^{v}	85.6 (2)	O2—Cl1—O3^{viii}	109.79 (19)
O1^{i}—Mg1—O1^{iii}	179.9 (3)	O2—Cl1—O3	109.79 (19)
O1^{iv}—Mg1—O1^{v}	179.9 (3)	O2—Cl1—O3^{ix}	109.79 (19)
O1^{vi}—Mg1—O1	179.9 (3)	O3—Cl1—O3^{viii}	109.15 (19)
O1^{iv}—Mg1—O1^{vi}	85.7 (2)	O3^{ix}—Cl1—O3	109.15 (19)

O1$^{\text{v}}$—Mg1—O1$^{\text{iii}}$	85.6 (2)	O3$^{\text{ix}}$—Cl1—O3$^{\text{viii}}$	109.15 (19)
O1—Mg1—O1$^{\text{iii}}$	85.6 (2)		

Symmetry codes: (i) $x-y$, x, $z-1/2$; (ii) $x-y$, x, $z+1/2$; (iii) $-x+y$, $-x$, z; (iv) y, $-x+y$, $z-1/2$; (v) $-y$, $x-y$, z; (vi) $-x$, $-y$, $z-1/2$; (vii) $-y$, $-x$, z; (viii) $-x+y+1$, $-x+1$, z; (ix) $-y+1$, $x-y$, z.