

Magnesium perchlorate anhydrate, $\text{Mg}(\text{ClO}_4)_2$, from laboratory X-ray powder data

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The previously unknown crystal structure of magnesium perchlorate anhydrate, determined and refined from laboratory X-ray powder diffraction data, represents a new structure type. The title compound was obtained by heating magnesium perchlorate hexahydrate at 523 K for 2 h under vacuum and it crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one Mg (site symmetry $\bar{1}$ on special position $2a$), one Cl and four O sites (on general positions $4e$). The structure consists of a three-dimensional network resulting from the corner-sharing of MgO_6 octahedra and ClO_4 tetrahedra. Each MgO_6 octahedron share corners with six ClO_4 tetrahedra. Each ClO_4 tetrahedron shares corners with three MgO_6 octahedra, with one O-atom corner dangling. The ClO_4 tetrahedra are oriented in such a way that one-dimensional channels parallel to $[100]$ are formed between the dangling O atoms.

Comment

The crystal structures of magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 6, 4, 2, 0$), have received much attention in order to understand the phase stabilities and reactivity of Martian soil, since perchlorate anions have been identified on the surface of Mars (Hecht *et al.*, 2009). Because of the oxidation state VII of chlorine, magnesium perchlorate is a very strong oxidizing agent, and it is commonly stabilized as a hexahydrate in the atmosphere with an orthorhombic structure ($Pmn2_1$) (West, 1935). The lower hydrates of magnesium perchlorate were reported by Besley & Bottomley (1969), confirmed later by Devlin & Herley (1986), and the crystal structures of the tetrahydrate (monoclinic, $C2$) and dihydrate (monoclinic, $C2/m$) forms were recently determined by Robertson & Bish (2010). However, the crystal structure of the anhydrous form, $\text{Mg}(\text{ClO}_4)_2$, has not been reported to date. We present here its crystal structure, as determined and refined from laboratory powder X-ray diffraction data (Fig. 1).

Anhydrous $\text{Mg}(\text{ClO}_4)_2$ crystallizes in a new structure type in terms of atomic ratios (1:2:8 for octahedral ion–tetrahedral

ion–oxygen) and its polyhedral network is, to the best of our knowledge, unique. The structure may be described as a three-dimensional polyhedral network resulting from the corner-sharing of highly regular MgO_6 octahedra and ClO_4 tetrahedra (Table 1). Each MgO_6 octahedron shares corners with six ClO_4 tetrahedra (Fig. 2*a*), as expected by Robertson & Bish (2010). Each ClO_4 tetrahedron shares corners with three MgO_6 octahedra, with one corner (O4) left dangling (Fig. 2*b*). The polyhedra are oriented in such a way that one-dimensional channels parallel to $[100]$ are formed in between the free O atoms, which are separated by about 3 Å (Table 1).

There is a systematic transformation of the crystal structures of $\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 6, 4, 2, 0$) as the number of H_2O molecules decreases. The unit-cell volume containing two formula units ($Z = 2$) is reduced from 553 ($n = 6$) to 505 ($n = 4$) to 388 Å³ ($n = 2$) and further to 282 Å³ ($n = 0$), as expected. For the hexahydrate ($n = 6$), the Mg^{2+} ion is coordinated by O atoms from six H_2O molecules, and each O atom in the perchlorate tetrahedron is hydrogen bonded to H_2O (West, 1935). In the tetrahydrate ($n = 4$), the Mg^{2+} ion is still octahedrally coordinated by O atoms, but only four of them are from H_2O molecules and the other two from ClO_4 tetrahedra. In the dihydrate ($n = 2$), the Mg^{2+} ion is coordinated by two H_2O molecules and four ClO_4 tetrahedra (Robertson & Bish, 2010). As we have now confirmed, in the anhydrate ($n = 0$), the Mg^{2+} ion is coordinated by six ClO_4 tetrahedra only. Presumably, the highly hygroscopic nature of the anhydrate arises from both the more exothermic hydration enthalpy of the Mg^{2+} cation compared with other metals (Wulfsberg, 1991) and the stabilization of $\text{O} \cdots \text{O}$ repulsion in the channels by hydrogen bonding.

The crystal structure of $\text{Mg}(\text{ClO}_4)_2$ is rather simple but, to the best of our knowledge, it appears to be a new structure type of the formula AB_2X_8 . The most closely related structures

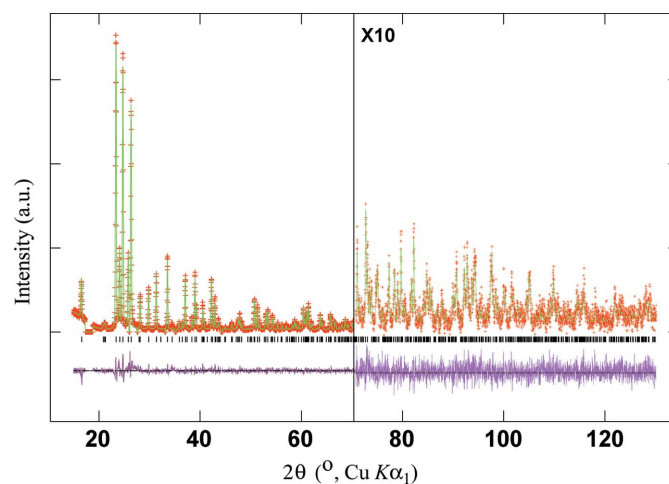


Figure 1
X-ray Rietveld refinement profiles for $\text{Mg}(\text{ClO}_4)_2$, excluding the minor impurity phase peaks (data recorded at room temperature). Crosses mark the experimental points (red in the electronic version of the paper) and the solid line is the calculated profile (green). The bottom trace shows the difference curve (purple).

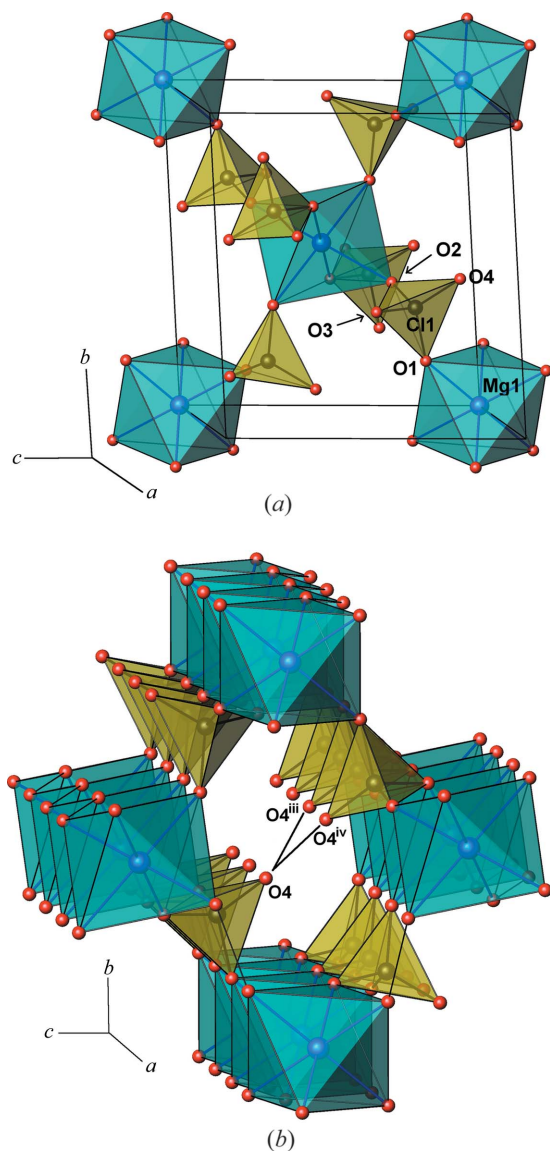


Figure 2

(a) The structure of $\text{Mg}(\text{ClO}_4)_2$, with MgO_6 octahedra (blue in the electronic version of the paper) and ClO_4 tetrahedra (yellow). (b) The one-dimensional channel parallel to $[100]$ between the dangling O4 atoms. [Symmetry codes: (iii) $-x, -y + 1, -z$; (iv) $-x + 1, -y + 1, -z$.]

would be those for $M^{2+}(\text{BO}_4)_2$ ($M = \text{Ni}$ or Co and $B = \text{Cl}$ or Re), which consist of MO_6 octahedra and BO_4 tetrahedra connected to each other by corner-sharing, similar to $\text{Mg}(\text{ClO}_4)_2$. The tetrahedron also has one dangling O atom. However, all the tetrahedra are aligned so that threefold symmetry is maintained; the perchlorates [Pascal *et al.*, 1985; ICSD (2009) Nos. 33288 (CoCl_2O_8) and 33289 (NiCl_2O_8)] and perrhenates [Butz *et al.*, 1998; ICSD Nos. 51015 (CoRe_2O_8) and 51016 (NiRe_2O_8)] have $R\bar{3}$ and $P\bar{3}$ space groups, respectively. The dangling O atoms form two-dimensional double layers parallel to the (001) plane in these compounds, clearly different from the one-dimensional cavities in $\text{Mg}(\text{ClO}_4)_2$.

The empirical expression for bond valence, which has been widely adopted to estimate valences in inorganic solids (Brown, 2002), was used to check the $\text{Mg}(\text{ClO}_4)_2$ crystal structure. The bond-valence sums (Brown & Altermatt, 1985;

Breese & O'Keeffe, 1991), calculated with the program *VALENCE* (Hormillosa *et al.*, 1993) for Mg (2.24 valence units, v.u.), Cl (6.94 v.u.), O1 (2.06 v.u.), O2 (2.04 v.u.), O3 (1.92 v.u.) and O4 (1.81 v.u.), match the expected charges of the ions reasonably well. Atom O4 has lowest valence sum since it has only a Cl–O bond.

Experimental

The anhydrous form of magnesium perchlorate was prepared by dehydration of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich). Magnesium perchlorate hexahydrate powder was thoroughly ground in an agate mortar and placed in the bottom of a fused-silica tube, with the other end sealed with a rubber septum. The tube was inserted into a box furnace through a hole at the top of the furnace, so that the sample end of the tube was at the centre of the furnace and the septum end outside, connected to a vacuum pump through a needle piercing the septum. The tube was heated at a rate of 4 K min^{-1} up to 523 K and held at this temperature for 2 h under continuous vacuum. After cooling, the powder sample used for X-ray measurement was processed in an Ar-atmosphere glove-box. A tightly sealed dome-type X-ray sample holder, commercially available from Bruker AXS, was used to prevent hydration during measurement. The powder X-ray diffraction (XRD) data were collected at room temperature on a Bragg–Brentano diffractometer (Bruker Advance D8) with a Cu X-ray tube, a focusing primary Ge(111) monochromator ($\lambda = 1.5405 \text{ \AA}$) and a position-sensitive Vantec detector with a 6° slit. Data acquisition covered the angular range $15^\circ \leq 2\theta \leq 130^\circ$ at a step width of 0.01668° and a total measurement time of 20 h.

Crystal data

$\text{Mg}(\text{ClO}_4)_2$	$V = 282.14 (1) \text{ \AA}^3$
$M_r = 223.20$	$Z = 2$
Monoclinic, $P2_1/c$	Cu $K\alpha_1$ radiation
$a = 4.85705 (10) \text{ \AA}$	$\lambda = 1.5405 \text{ \AA}$
$b = 8.41719 (16) \text{ \AA}$	$T = 296 \text{ K}$
$c = 7.87301 (16) \text{ \AA}$	Flat sheet, $20 \times 20 \text{ mm}$
$\beta = 118.7704 (11)^\circ$	

Data collection

Bruker D8 Advance diffractometer	Scan method: step
Specimen mounting: packed powder	$2\theta_{\min} = 15.0^\circ$, $2\theta_{\max} = 129.989^\circ$,
Data collection mode: reflection	$2\theta_{\text{step}} = 0.017^\circ$

Refinement

$R_p = 0.102$	$R(F^2) = 0.0875$
$R_{\text{wp}} = 0.145$	$\chi^2 = 1.823$
$R_{\text{exp}} = 0.107$	6894 data points
$R_{\text{Bragg}} = 0.087$	32 parameters

Structure determination from the powder XRD data was performed using a combination of the powder profile refinement program *GSAS* (Larson & Von Dreele, 2000) and the single-crystal structure refinement program *CRYSTALS* (Betteridge *et al.*, 2003). For a three-dimensional view of the Fourier density maps, *MCE* was used (Rohlíček & Hušák, 2007). The XRD pattern was indexed using the program *TREOR90* (Werner, 1990) run in *CRYSTFIRE* (Shirley, 2002) via the positions of 19 diffraction peaks after excluding the impurity phase peaks, resulting in a monoclinic unit cell. The systematic absences suggested the space group $P2_1/n$ (No. 14). The unit cell and space group are consistent with the results reported previously for an unidentified hydrate form of magnesium perchlo-

Table 1

Selected geometric parameters (Å, °).

Mg1—O1	2.081 (4)	Cl1—O3	1.463 (4)
Mg1—O2 ⁱ	2.121 (5)	Cl1—O4	1.412 (5)
Mg1—O3 ⁱⁱ	2.092 (4)	O4—O4 ⁱⁱⁱ	2.889 (8)
Cl1—O1	1.434 (4)	O4—O4 ^{iv}	3.175 (9)
Cl1—O2	1.431 (4)		
O1—Mg1—O2 ⁱ	86.43 (16)	O1—Cl1—O4	114.3 (3)
O1—Mg1—O3 ⁱⁱ	91.78 (17)	O2—Cl1—O3	110.0 (3)
O2 ⁱ —Mg1—O3 ⁱⁱ	86.37 (16)	O2—Cl1—O4	109.8 (3)
O1—Cl1—O2	106.9 (3)	O3—Cl1—O4	111.5 (3)
O1—Cl1—O3	104.2 (3)		

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

rate (Visser, 1979; JCPDS PDF card No. 31-0789). The unit cell was transformed so as to conform to the conventional space group $P2_1/c$. There were some minor impurity peaks with much broader peak widths, all of which are consistent with the peak positions reported for an unidentified decomposed phase of magnesium perchlorate (Hanawalt *et al.*, 1938; JCPDS PDF card No. 1-0629). Since most of the impurity peaks did not overlap with the main ones, they were excluded in the structure determination and refinement. The structure determination was performed in the same way as in previous work (Lee & Hong, 2008). At the beginning, a structural model with only a dummy atom at an arbitrary position in the unit cell was used. Structure factors were extracted from the powder data, and then direct methods were used for the initial solution of the structure using *SHELXS97* (Sheldrick, 2008) run in *CRYSTALS*, which yielded several atom positions. Due to the high-quality XRD data and the relatively simple structure, all six atoms could be identified and a satisfactory structural model was obtained at once. Finally, Rietveld refinement was employed to complete the structure determination, resulting in reasonable isotropic displacement parameters and agreement indices.

Data collection: *COMMANDER* (Bruker, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 2000); data reduction: *EVA* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to

refine structure: *GSAS*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *GSAS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3289). Services for accessing these data are described at the back of the journal.

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