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Synthesis and crystal structure of magnesium chlorate dihydrate and magnesium chlorate hexahydrate

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Two magnesium chlorate hydrates, $Mg(ClO_3)_2 \times 6(H_2O)$ (**1**) and $Mg(ClO_3)_2 \times 2(H_2O)$ (**2**), have been synthesized by slow evaporation from water and ethanol, respectively. The structures were determined by single-crystal X-ray diffraction at 150 K due to the dehydration-rehydration at room temperature leading to multiple phase transitions. Both compounds crystallized in the monoclinic space group $P2_1/c$ (SG 14) with respective unit cell parameters of $a = 6.3899(3)$, $b = 6.5139(3)$, $c = 13.8963(6)$Å, $\beta = 100.319(5)°$, $V = 569.05(5)$ Å^3, $Z = 2$, $R = 0.0210$ and $a = 6.3707(5)$, $b = 5.4092(3)$, $c = 9.8208(6)$ Å, $\beta = 97.338(6)°$, $V = 335.66(4)$ Å^3, $Z = 2$, $R = 0.0201$. The structure solution shows an octahedral coordination of the Mg^{2+} for both compounds **1** and **2**. In the case of $Mg(ClO_3)_2 \times 6(H_2O)$ the coordination is achieved by the water molecules, while for $Mg(ClO_3)_2 \times 2(H_2O)$ the coordination involves two water molecules and is complemented by four oxygen atoms from the chlorate moiety.

Key words: magnesium chlorate, hydrates, single crystal.

INTRODUCTION

The coordination chemistry of magnesium is well studied because of its role and participation in a multitude of reactions in the living organisms. Magnesium is an essential component of many enzymes [1]. It binds and thus activates ATP and participates in the process of energy transfer and construction of nucleic acids [2]. The preferred coordination number of magnesium is six [3]. In the majority of known crystal phases involving the participation of magnesium it favors the octahedral coordination.

With the discovery of perchlorates ClO_4^- on Mars by NASA *Phoenix Lander* [4] the interest in studying and modeling the oxidized forms of chlorine increased. Between the chloride (oxidation state –1) and perchlorate (oxidation state +7) there are three other ions – hypochlorite ClO^- (oxidation state +1), chlorite ClO_2^- (oxidation state +3) and chlorate ClO_3^- (oxidation state +5). Chlorates are of peculiar interest due to their stability [5], though, their structural and crystallographic characteristics are similar to those of perchlorates. Alkali or alkaline earth metal chlorates are intensively studied, mostly sodium and magnesium chlorates, which is reasoned by the distribution of those elements in nature and the low eutectic temperatures of the aqueous solutions of $Mg(ClO_3)_2$. Magnesium chlorates have different industrial applications: in paper production; in agro chemistry as herbicide and defoliant; in pyrotechnics; and as antiseptic agent [6].

The first communication about magnesium chlorate hexahydrate was made by Wachter [7], who obtained it in 1841 from the reaction of barium chlorate and magnesium sulfate. Later, Meusser [8] determined the temperature at which $(Mg(ClO_3)_2).6H_2O$ melts in its crystallization water to be 35 °C. In addition to the hexahydrate, magnesium chlorate forms two other crystal hydrates with two (compound **2**) and four water molecules. The phase diagram of the system magnesium chlorate – water was reported by Linke in 1965 [9]. The tetrahydrate form $(Mg(ClO_3)_2).4H_2O$ is stable in the temperature range 35–65 °C, while above that temperature the stable form is $(Mg(ClO_3)_2).2H_2O$.

While the chemical and physicochemical properties of the anhydrous magnesium chlorate, as well as its hydrate forms have been well studied, the crystal structure(s) of none the salts were determined. In this study we report the crystal structures of two of the three magnesium hydrates

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namely $Mg(ClO_3)_2\times6(H_2O)$, (compound **1**) and $Mg(ClO_3)_2\times2(H_2O)$ (compound **2**).

MATERIALS AND METHODS

Synthesis

Magnesium chlorates were obtained via the reaction of barium chlorate monohydrate and magnesium sulfate heptahydrate [7] in equimolar ratio, followed by recrystallization in ethanol solution.

Synthesis of compound 1

Barium chlorate monohydrate (0.322 g, 1.0 mmol) was dissolved in 20 ml distilled water. Magnesium sulfate heptahydrate (0.246 g, 1.0 mmol) was dissolved in 20 ml distilled water. The water solution of magnesium sulfate heptahydrate was slowly added to the barium one under constant stirring. After three hours the mixture is centrifuged for 30 min at 5000 rpm. The barium sulfate pellet was discarded while the supernatant is transferred to a rotary evaporator. The obtained magnesium chlorate was recrystallized in 5 ml ethanol.

Colorless single crystals of magnesium chlorate hexahydrate, $Mg(ClO_3)_2.6H_2O$ (compound **1**), were grown by slow evaporation from an aqueous solution at room temperature.

Synthesis of compound 2

The synthesis of compound **2** followed the same steps as described for compound **1**. Colorless single crystals of magnesium chlorate dehydrate, $Mg(ClO_3)_2.2H_2O$ (compound **2**), were grown by slow evaporation from absolute ethanol at room temperature.

Single crystal X-ray diffraction study

Crystals of compounds **1** and **2** suitable for single crystal XRD analysis were placed on a glass fiber and mounted on an Agilent, SuperNovaDual four-circle diffractometer equipped with Atlas CCD detector and using mirror-monochromatized MoKα ($\lambda = 0.7107$ Å) radiation from a micro-focus source. The crystals were flash frozen at 150 K in an N_2 gas stream (Cobra, Oxford cryosystems) and diffraction data were collected at this temperature by ω-scan technique. The determination of cell parameters, data integration, scaling and absorption correction were carried out using the CrysAlisPro program package [10]. The structures were solved by direct methods using ShelxS [11] and refined by full-matrix least-square procedures on F^2 with ShelxL-97 [11]. The hydrogen atoms were located from difference Fourier map and refined as riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(O)$.

RESULTS AND DISCUSSION

The crystal structures of the magnesium chlorate hydrates (di-, tetra- and hexa- hydrates) have not been reported although the synthesis of these three magnesium chlorates has been published [12]. The performed check (ICDD-PDF and ICSD) revealed that similar magnesium chlorates (where the water is replaced by another small highly polar molecule e.g. urea) have been characterized.

The structures of some magnesium oxychlorides have also been reported ($Mg(ClO_4)_2.6H_2O$) [13] and ($Mg(ClO_2)_2.6H_2O$) [14]). The problem with the crystal structure determination of magnesium chlorates is associated with their relative instability at ambient temperature. Actually, the performed room temperature data collection resulted in good diffraction of the crystals for 10–15 minutes after what diffraction disappeared almost instantly. The attempted X-ray powder data collection was also unsuccessful. Thus we performed single crystal data collection by flash freezing the crystals in N_2 at 150 K.

An *ORTEP* view with 50% probability of the molecular structures of compounds **1** and **2** and the atom numbering scheme is shown in Figure 1. The experimental conditions are summarized in Table 1.

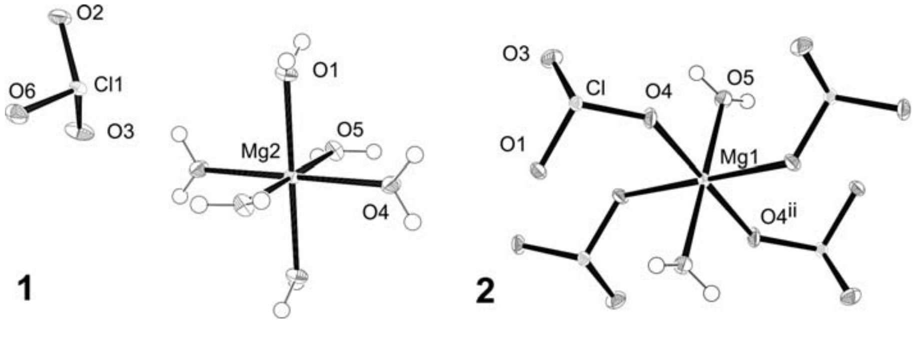

Fig. 1. View of the molecular structures of compounds **1** and **2** with atomic numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The H atoms are presented with spheres with arbitrary radii

Table 1. Crystal data and most important refinement indicators for compounds **1** and **2**

	1	**2**
Empirical formula	$Cl_2H_{12}MgO_{12}$	$Cl_2H_4MgO_8$
Molecular weight	299.31	227.24
Crystal size (mm)	0.32 × 0.30 × 0.28	0.23 × 0.21 × 0.18
Crystal habit, color	prism, colorless	prism, colorless
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
T(K)	150	150
Radiation wavelength (E)	0.71073 (Mo K*a*)	0.71073 (Mo K*a*)
a (E)	6.3899(3)	6.3707(5)
b (E)	6.5139(3)	5.4092(3)
c (E)	13.8963(6)	9.8208(6)
α (°)	90	90
β (°)	100.319(5)	97.338(6)
γ (°)	90	90
V (E^3)	569.05(5)	335.66(5)
Z	2	2
d (mg. m^{-3})	1.747	2.248
μ (mm^{-1})	0.67	1.06
diffractometer	Agilent SupernovaDual	Agilent SupernovaDual
Detector, resolution mm^{-1}	Atlas CCD, 10.3974 pixels	Atlas CCD, 10.3974 pixels
radiation source, wavelength (Å)	Mova(Mo) X-ray source, $\lambda = 0.7107$	Mova(Mo) X-ray source, $\lambda = 0.7107$
Absorption correction	multi-scan, CrysAlisPro	multi-scan, CrysAlisPro
Refinement, Least-squares matrix	F^2, Full	F^2, Full
Reflections collected/I>2σ (I)	3955/1288	1388/788
parameters	94	61
R1 ($F^2 > 2\sigma(F^2)$)	0.021	0.02
wR2 (all data)	0.057	0.055
GOF	1.08	0.83
Extinction correction	none	0.049(5)
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.32/–0.45	0.23/–0.33

Table 2. Selected geometrical parameters for compounds **1** and **2** (Å, °)

Bond distance			
compound 1		compound 2	
Cl1 — O2	1.4923(8)	Cl1 — O1	1.5019 (9)
Cl1 — O3	1.4808(9)	Cl1 — O3	1.4793(11)
Cl1 — O6	1.4843(8)	Cl1 — O4	1.4850 (9)
Mg2 — O1	2.0481(8)	Mg1 — O1	2.1039(9)
Mg2 — O4	2.0455(8)	Mg2 — O4	2.0733(10)
Mg2 — O5	2.0703(8)	Mg2 — O5	2.0429(10)
Bond angle			
O1— Mg2 — O5	88.07(3)/91.93(3) ^{i}	O5— Mg1 — O1	89.48(4)/90.52(4)^{ii}
O4— Mg2 — O1	90.62(4)/89.38(4)^{i}	O5— Mg1 — O4	88.96(4)/91.04(4)^{ii}
O4— Mg2 — O5	90.45(4)/89.55(4)^{i}	O4— Mg1 — O1	88.05(4)/91.95(4)^{ii}
O3 —Cl1 — O2	107.25(5)	O1— Cl — O3	105.98(6)
O3 —Cl1 — O6	106.62(5)	O1— Cl — O4	106.48(6)
O6 —Cl1 — O2	107.19(5)	O3— Cl — O4	107.41(6)

Symmetry operations: (i) $-x, -y, -z+1$; (ii) $x, y, z-1$.

Selected bond distances and bond angles are listed in Table 2. Hydrogen bonding geometry is presented in Table 3. The data for publication were prepared with WinGX [15], *ORTEP* [16], and Mercury [17] program packages.

As expected, the crystal structure of the hexahydrate consists of discrete $[Mg(H_2O)6]^{2+}$ octahedra and chlorate anions (Fig. 2). The $[Mg(H_2O)6]^{2+}$ octahedra are connected via hydrogen bonds to chlorate anions, where every H atom of the six water

Table 3. Hydrogen bond for compounds **1** and **2** (Å, °)

D—H···A	D—H	d(H···A)	d(D···A)	<(DHA)
Compound **1**				
O1—H1A···O6^{i}	0.801	2.084	2.879(5)	172.0
O1—H1B···O3^{i}	0.804	1.957	2.763(5)	160.7
O4—H4A···O6^{ii}	0.804	1.951	2.739(4)	166.6
O4—H4B ···O2^{iii}	0.809	2.038	2.845(5)	175.3
O5—H5A ···O3^{i}	0.775	2.120	2.886(5)	170.3
O5—H5B···O2^{iv}	0.822	2.087	2.901(5)	177.5
Compound **2**				
O5—H1···O3^{v}	0.751	2.094	2.843(5)	168.8
O5—H2···O3^{vi}	0.745	2.267	2.942(5)	151.2

Symmetry codes : (i) *–x, –1/2+y, 1/2–z*; (ii) *–1+x, 1/2–y, 1/2+z*; (iii) *1–x, -y, 1–z*; (iv) *–1+x, 1/2–y, 1/2+z*; (v) *–1+x, y, z* (vi) *1–x, 1–y, 2–z*.

molecules is in contact with a chlorate anions, with a O…O distances in the range of 1.95–2.15 Å (Table 3), thus arranging 10 chlorate anions around the octahedral unit (Fig. 2). The result is the appearance of a complex three-dimensional hydrogen-bonding network comprising layers of chlorates anions and $[Mg(H_2O)6]^{2+}$ octahedra (Fig. 3).

In compound **2** the Mg coordination is also octahedral. However, in compound **2** a chlorate oxygen participates in the Mg coordination sphere. The magnesium atom (ion) and four chlorate ions lie in one plane, while the water molecules are in axial positions and Mg–O bonds are nearly perpendicular to this plane (89.44(5)°). The chlorate molecule acts as a bridge between two magnesium atoms (Mg–O–ClO–O–Mg) and thus produces layers that are stacked along *a*. The layers are stabilized by internal hydrogen bonds involving water molecules, O5 and chlorate O3. The three-dimensional stabilization of the structure is achieved by a bicyclic hydrogen O5-H…O3 between the adjacent layers (Fig. 4).

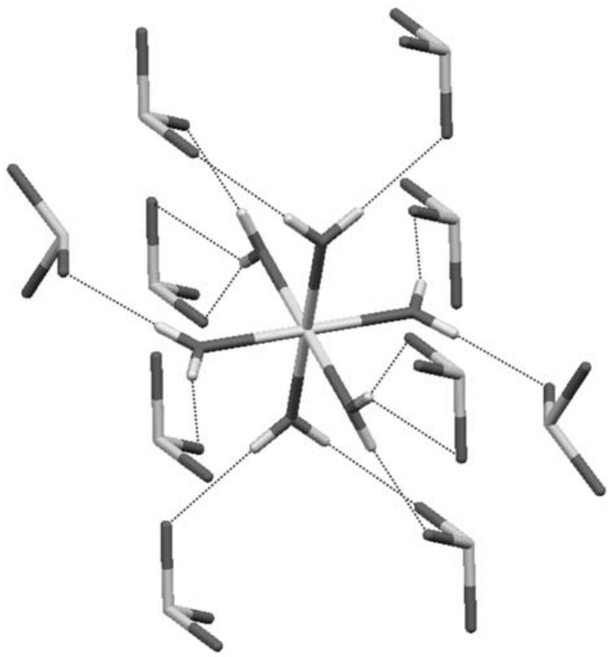

Fig. 2. Hydrogen bonding motif of $Mg(ClO_3)_2 \times 6(H_2O)$

CONCLUSIONS

The crystal structures of two elusive magnesium compounds, $Mg(ClO_3)_2 \times 6(H_2O)$ and $Mg(ClO_3)_2 \times 2(H_2O)$ were determined. They will help in the understanding of the rapid hydration processes and multiple phase transitions associated with magnesium hydrates and solvates.

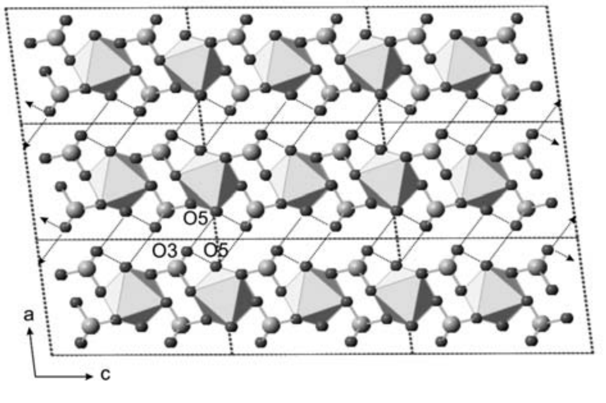

Fig. 3. Three-dimensional hydrogen-bond networks comprising layers of chlorates anions and $[Mg(H_2O)6]^{2+}$ octahedra

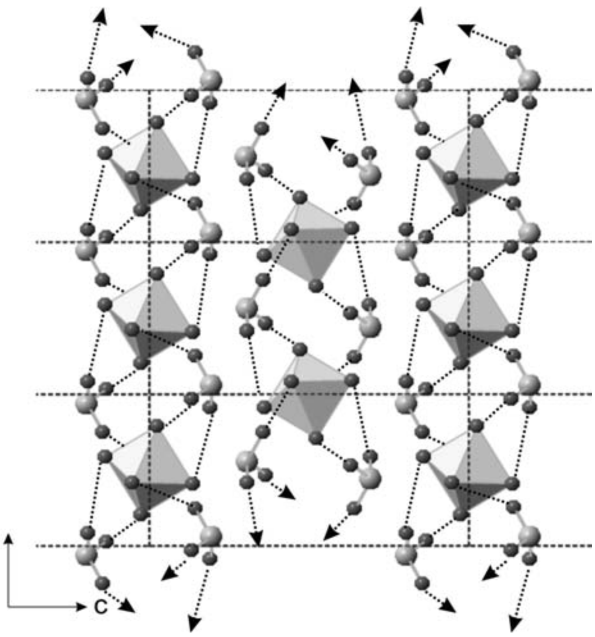

Fig. 4. Three-dimensional stabilization of the structure is achieved by a bicyclic hydrogen O5-H…O3 between the layers

SUPPLEMENTARY MATERIALS

ICSD 425637 and 425637 contain the supplementary crystallographic data for this paper. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate ICSD number.

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СИНТЕЗ И КРИСТАЛНА СТРУКТУРА НА МАГНЕЗИЕВ ХЛОРАТ ДИХИДРАТ И МАГНЕЗИЕВ ХЛОРАТ ХЕКСАХИДРАТ

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(Резюме)

Получени са монокристални образци на магнезиев хлорат $Mg(ClO_3)_2{\times}6(H_2O)$ (**1**) и $Mg(ClO_3)_2{\times}2(H_2O)$ (**2**) при условията на бавно изпарение, съответно от вода (**1**) и етанол (**2**). Поради ниската устойчивост на кристалите на стайна температура монокристалният експеримент е осъществен на 150 K. Рентгеноструктурният анализ разкрива, че двете съединения кристализират в моноклинната $P2_1/c$ пространствена група (No 14) с параметри на елементарната клетка $a = 6.3899(3)$, $b = 6.5139(3)$, $c = 13.8963(6)$ Å, $\beta = 100.319(5)°$, $V = 569.05(5)$ Å^3 и $a = 6.3707(5)$, $b = 5.4092(3)$, $c = 9.8208(6)$ Å, $\beta = 97.338(6)°$, $V = 335.66(4)$ Å^3. Рафинирането на кристалната структура показа, че Mg^{2+} е октаедрично координиран и при двете съединения. При $Mg(ClO_3)_2{\times}6H_2O$ координацията е само от водни молекули, докато при $Mg(ClO_3)_2{\times}2(H_2O)$ координационният октаедър включва две молекули вода, а останалите четири позиции се заемат от кислородни атоми на хлоратни йони.