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Magnesium chloride tetrahydrate, $MgCl_2·4H_2O$

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The title compound, $MgCl_2·4H_2O$, was crystallized at 403 K and its structure determined at 200 K. The structure is built up from $MgCl_2(H_2O)_4$ octahedra with a *trans* configuration. Each complex is situated on a crystallographic twofold axis, with the rotation axis aligned along one $H_2O—Mg—OH_2$ axis. They are connected by a complex network of O—H···Cl hydrogen bonds. The structure contains two-dimensional sections that are essentially identical to those in the reported tetrahydrates of $CrCl_2$, $FeCl_2$, $FeBr_2$ and $CoBr_2$, but they are stacked in a different manner in $MgCl_2·4H_2O$ compared with the transition metal structures.

Comment

Recently, Sugimoto *et al.* (2007) reported a crystal structure of $MgCl_2·4H_2O$ from *in situ* synchrotron powder diffraction experiments during dehydration of $MgCl_2·6H_2O$. Under these conditions, the tetrahydrate represents an intermediate phase between $MgCl_2·6H_2O$ and lower hydrates in the dehydration process, and the degree of equilibration is dependent on the heating rate and the pressure of the water vapour. A highly disordered structure was found, where only every second $MgCl_2(H_2O)_4$ octahedron is occupied. We report here an ordered crystal structure for $MgCl_2·4H_2O$, obtained from single-crystal data under equilibrium conditions.

$MgCl_2·4H_2O$ crystallizes as a stable phase between 390 and 454 K, in accordance with the phase diagram of the $MgCl_2$–H_2O system (Fanghänel *et al.*, 1987). The structure is built up from octahedral $MgCl_2(H_2O)_4$ units with the Cl atoms in *trans* positions, as shown in Fig. 1. The complexes lie on crystallographic twofold axes, aligned along the O1—Mg1—O3 axis. Although there is only one unique crystallographic position for the Mg and Cl atoms, two different orientations of the $MgCl_2(H_2O)_4$ octahedra exist. Viewing the structure parallel to the *b* axis (Fig. 2), adjacent rows of octahedra possess alternating orientations of their Cl—Mg—Cl axes, giving rise to a zigzag pattern along the *a* axis. Consequently, the $Mg(H_2O)_4$ planes also have alternating orientations with an angle of nearly 90° between them. However, there are no hydrogen bonds between the water molecules of nearest-neighbour planes. Instead, all the octahedra are interconnected by O—H···Cl hydrogen bonds (Table 1 and Fig. 3). The $Mg(H_2O)_4$ coordination planes contain two types of water molecules: one type (O1 and O3) in a 'dipole orientation' and the other (O2) tilted from the $Mg(H_2O)_4$ plane by *ca* 30° (Fig. 1). 'Dipole orientation' means that the water molecules and Mg atoms are located in one plane, and the Mg—O axis bisects the H—O—H angle. The tilted water molecules form shorter hydrogen bonds towards adjacent Cl atoms (Table 1 and Fig. 3). Each H atom of an $Mg(H_2O)_4$ plane forms one hydrogen bond to an adjacent Cl atom of a different $MgCl_2(H_2O)_4$ octahedron, resulting in connections to eight octahedra (Fig. 3). Each Cl atom acts as an acceptor for four

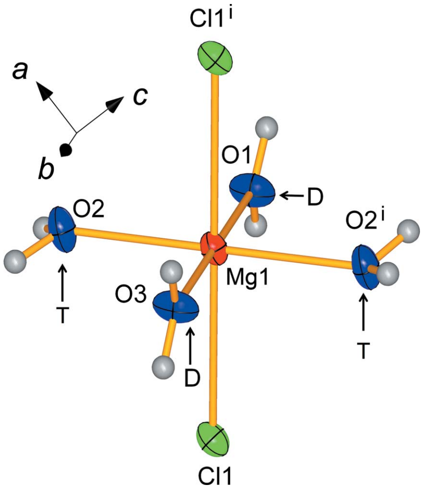

Figure 1
The $MgCl_2(H_2O)_4$ octahedron, showing displacement ellipsoids at the 50% probability level. The labels 'T' and 'D' refer to tilted and dipole orientations of the water molecules, respectively, as discussed in the *Comment*. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

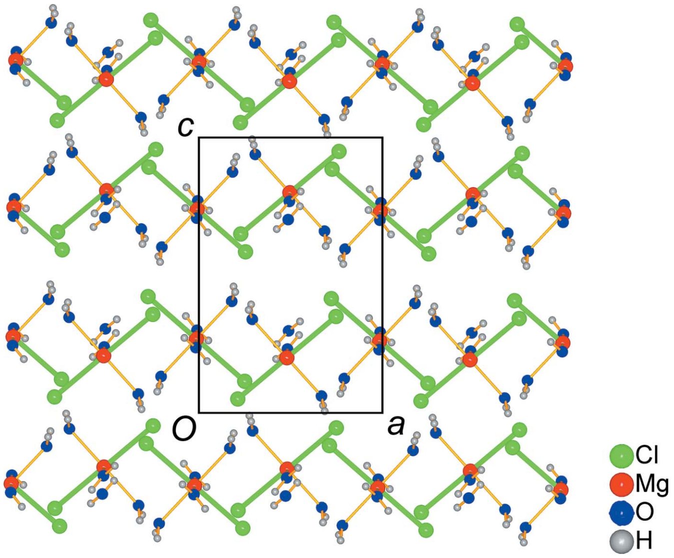

Figure 2
A packing diagram, viewed along the *b* axis, showing the zigzag arrangement of Cl—Mg—Cl axes along the *a* axis.

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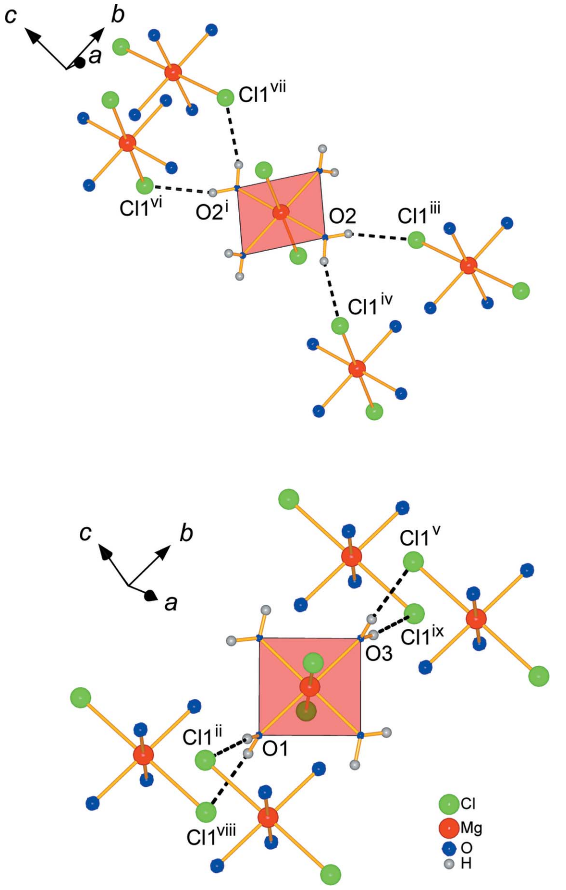

Figure 3
The hydrogen-bonding pattern (dashed lines) for the tilted water molecules (top) and the dipole orientation (bottom). [Symmetry codes are as in Table 1; additionally: (i) $-x + 1, y, -z + \frac{1}{2}$; (vi) $x, -y + 2, z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (ix) $-x + \frac{1}{2}, y + \frac{1}{2}, z$.]

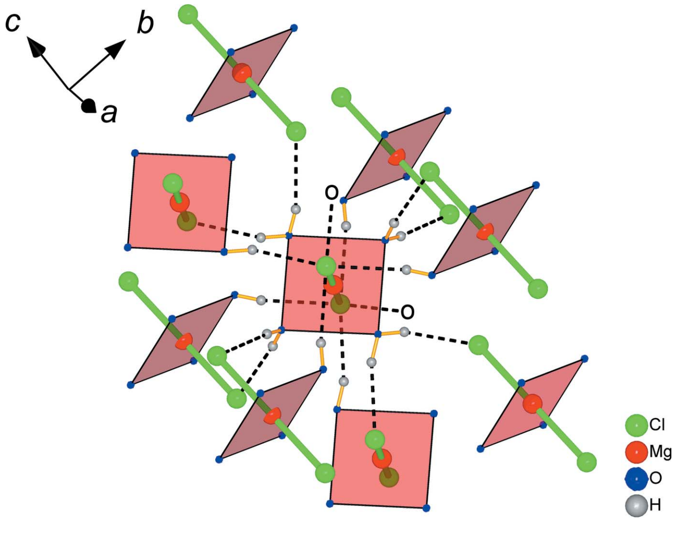

Figure 4
The hydrogen bonds (dashed lines) formed to the Cl atoms at one $MgCl_2(H_2O)_4$ octahedron. For clarity, two octahedra corresponding to the H atoms indicated by open circles are not drawn. The central octahedron is connected in total to ten neighbouring octahedra.

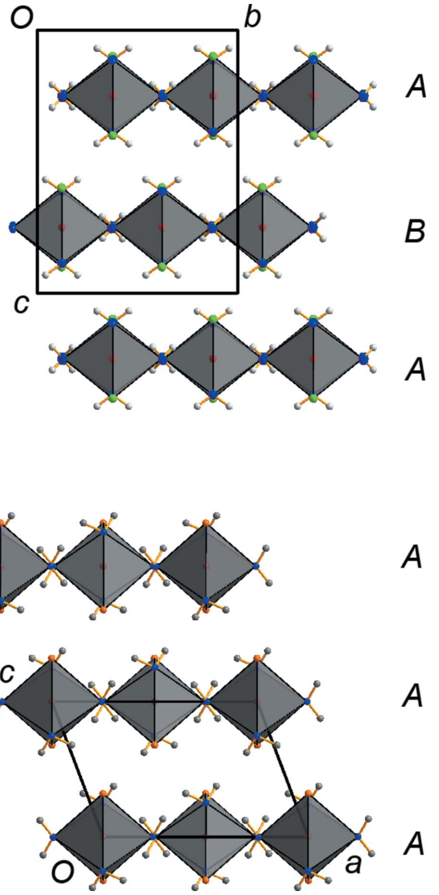

Figure 5
A polyhedral representation of $MgCl_2{\cdot}4H_2O$ (top) and $FeBr_2{\cdot}4H_2O$ (bottom; data from Waizumi *et al.*, 1992). The horizontal layers of octahedra are essentially identical in the two structures. Stacking of the layers in $MgCl_2{\cdot}4H_2O$ can be described as an *ABAB* sequence, compared with an *AAA* sequence in $FeBr_2{\cdot}4H_2O$.

hydrogen bonds, as illustrated in Fig. 4. Three of these are formed with water molecules from already connected octahedra (as shown in Fig. 3), while the fourth hydrogen bond extends to an additional $MgCl_2(H_2O)_4$ octahedron. Thus, each octahedron is connected to ten others, yielding a complicated hydrogen-bond network.

The *trans* configuration observed in $MgCl_2{\cdot}4H_2O$ has also been reported for $FeCl_2{\cdot}4H_2O$ (Meunier-Piret & Van Meerssche, 1971), $CrCl_2{\cdot}4H_2O$ (Von Schnering & Brand, 1973), and $CoBr_2{\cdot}4H_2O$ and $FeBr_2{\cdot}4H_2O$ (Waizumi *et al.*, 1992), whereas the tetrahydrates of $MnCl_2$ (Hwang & Ha, 2009), $MnBr_2$ (Sudarsanan, 1975), $CoCl_2$ (Waizumi *et al.*, 1990) and $NiCl_2$ (Ptasiewicz-Bak *et al.*, 1999; Waizumi *et al.*, 1992) crystallize with the Cl atoms in a *cis* configuration. For the structures with a *trans* configuration, $MgCl_2{\cdot}4H_2O$ provides a structure reference for a cation without any *d*-electron effects. $FeCl_2{\cdot}4H_2O$ (space group $P2_1/c$), $CrCl_2{\cdot}4H_2O$ ($P2_1/c$), $CoBr_2{\cdot}4H_2O$ ($P2_1/a$) and $FeBr_2{\cdot}4H_2O$ ($P2_1/a$) are isomorphous with each other, although reported with two different cell settings. In contrast, $MgCl_2{\cdot}4H_2O$ crystallizes in the orthorhombic space group *Pbcn*. Comparing, for example, the crystal structures of $MgCl_2{\cdot}4H_2O$ and $FeBr_2{\cdot}4H_2O$, as shown in Fig. 5, identical layers of $MX_2(H_2O)_4$ octahedra can be recognized.

However, there is a distinction between the stacking arrangements of the layers. In $FeBr_2 \cdot 4H_2O$, they are stacked by translation along the lattice vector **c**. This type of stacking is referred to as *AAA*. In $MgCl_2 \cdot 4H_2O$, the layer stacking is of the type *ABAB*, with each layer offset laterally by $\frac{1}{2}b$ compared with the Fe compound. This can also be viewed as a reflection of adjacent layers, with the mirror plane perpendicular to the *a* axis, at $x = 0.25$ and 0.75. This difference in stacking is expressed by the different space groups. Possibly, these different stackings are caused by small differences in the orientation of the water molecules in the $MX_2(H_2O)_4$ octahedra, and a more symmetric orientation is evident in the case of $MgCl_2 \cdot 4H_2O$. The interplay between the energetic states of the *d* electrons in the ligand fields and the requirements for hydrogen bonding reduces the symmetry in the case of the transition metal halide hydrates. A similar situation was reported recently by Schau-Magnussen *et al.* (2011) for hexaaquamagnesium (space group *Pbca*) and hexaaquanickel(II) furan-2,5-dicarboxylates ($P2_1/c$).

Experimental

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Fluka, >98%) was heated in a flask at 403 K. The flask was closed with a cork stopper, which was pierced with a glass capillary for water discharge. The sample was held for 48 h at that temperature, and single crystals were formed on the surface of the dehydrated melt. The crystals were separated from a solidified hydrate melt. To prevent contact of the crystals with humidity in the air, they were coated with *n*-paraffin oil. The crystal selected for data collection was embedded in silicone oil before being mounted on the diffractometer.

Crystal data

$MgCl_2 \cdot 4H_2O$
$M_r = 167.27$
Orthorhombic, *Pbcn*
$a = 7.2557$ (3) Å
$b = 8.4285$ (4) Å
$c = 11.0412$ (6) Å
$V = 675.22$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.98$ mm^{-1}
$T = 200$ K
0.5 × 0.4 × 0.3 mm

Data collection

Stoe IPDS 2T diffractometer
Absorption correction: integration (Coppens, 1970)
$T_{min} = 0.791$, $T_{max} = 0.907$
62835 measured reflections
1488 independent reflections
1212 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.051$
$S = 1.06$
1482 reflections
50 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$O1—H3 \cdots Cl1^{ii}$	0.817 (13)	2.400 (13)	3.2097 (4)	171.5 (12)
$O2—H1 \cdots Cl1^{iii}$	0.858 (13)	2.345 (13)	3.1751 (4)	163.0 (10)
$O2—H2 \cdots Cl1^{iv}$	0.819 (14)	2.380 (14)	3.1789 (4)	165.2 (12)
$O3—H4 \cdots Cl1^{v}$	0.793 (13)	2.431 (14)	3.2160 (4)	170.8 (12)

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

All H atoms were located in Fourier maps and refined freely with isotropic displacement parameters.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3028). Services for accessing these data are described at the back of the journal.

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