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# Lithium carnallite, $LiCl\cdot MgCl_2\cdot 7H_2O$

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The title compound, lithium magnesium chloride heptahydrate, $LiCl\cdot MgCl_2\cdot 7H_2O$, was analyzed in 1988 by powder X-ray diffraction [Emons, Brand, Pohl & Köhnke (1988). *Z. Anorg. Allg. Chem.* **563**, 180–184] and a monoclinic crystal lattice was determined. In the present work, the structure was solved from single-crystal diffraction data. A trigonal structure was found, exhibiting a network structure of $Mg(H_2O)_6$ octahedra and $Li(H_2O)Cl_3$ tetrahedra connected by H···Cl hydrogen bonds. The $[Li(H_2O)]^+$ unit is coordinated by distorted edge-connected $Cl^-$ octahedra.

## Comment

$LiCl\cdot MgCl_2\cdot 7H_2O$ belongs to the group of double salts $MX\cdot MgX_2\cdot 6H_2O$, with $M$ = $[Li(H_2O)]^+$, $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$ and $H_3O^+$, and $X$ = $Cl^-$, $Br^-$ and $I^-$. The most important member of this group is the mineral carnallite, *viz.* $KCl\cdot MgCl_2\cdot 6H_2O$. Carnallite is formed during evaporation of potassium- and magnesium-rich waters. It belongs to the family of natural salts and has applications as a source for potash fertilizer production and in the recovery of magnesium chloride.

The structure analysis of $LiCl\cdot MgCl_2\cdot 7H_2O$ is motivated by a growing interest in natural lithium resources for battery materials. Lithium carnallite is formed during evaporation from brines from salt lakes in South America.

In order to study the crystal chemistry of $MX\cdot MgX_2\cdot 6H_2O$ compounds, Emons *et al.* (1988) performed powder diffraction experiments on all of the above-mentioned carnallites, except $(H_3O)X\cdot MgX_2\cdot 6H_2O$, and published lattice parameters ($a$ = 9.223 Å, $b$ = 9.689 Å, $c$ = 13.371 Å and $\beta$ = 93.33° in the space group $C2/m$ for $LiCl\cdot MgCl_2\cdot 7H_2O$). Crystal structures were determined for $KCl\cdot MgCl_2\cdot 6H_2O$ (Fischer, 1973; Schlemper *et al.*, 1985), $NH_4Cl\cdot MgCl_2\cdot 6H_2O$ (Nakayasu, 1983; Solans *et al.*, 1983; Marsh, 1992*b*), $RbCl\cdot MgCl_2\cdot 6H_2O$ (Waizumi, Masuda, Ohtaki, Burkov & Scripkin, 1991; Marsh, 1992*a*), $CsCl\cdot MgCl_2\cdot 6H_2O$ (Waizumi, Masuda & Ohtaki, 1991), and $RbBr\cdot MgBr_2\cdot 6H_2O$ and $CsBr\cdot MgBr_2\cdot 6H_2O$ (Dinnebier *et al.*, 2008).

As shown in Fig. 1, the structure of $LiCl\cdot MgCl_2\cdot 7H_2O$ (lattice parameters $a$ = 9.2322 (3) Å and $c$ = 12.0541 (5) Å, space group $R3$) consists of $Mg(H_2O)_6$ octahedra and $Li(H_2O)Cl_3$ pseudo-tetrahedra. Atoms Li1, Mg1 and O3 are located on special positions of symmetry 3. The dumbbell-shaped $[Li(H_2O)]^+$ unit is oriented with the bonding axis parallel to the threefold symmetry axis. The vertices of the $Li(H_2O)Cl_3$ tetrahedra are three symmetry-related $Cl^-$ atoms and one water molecule, where the two H atoms of the water molecule are distributed equally over three energetically equivalent positions. Typical for $MX\cdot MgX_2\cdot 6H_2O$ structures, but not necessarily expected for $LiCl\cdot MgCl_2\cdot 7H_2O$, is the octahedral coordination of $M$ by $Cl^-$. Considering the $[Li(H_2O)]^+$ unit as coordination center, a distorted $Li(H_2O)Cl_6$ octahedron with three Li···Cl bonds of 2.3806 (10) Å and two H···Cl hydrogen bonds of 2.53 (5) Å results, as presented in Fig. 2. The $Li(H_2O)Cl_6$ octahedra form an edge-connected three-dimensional network. The structure

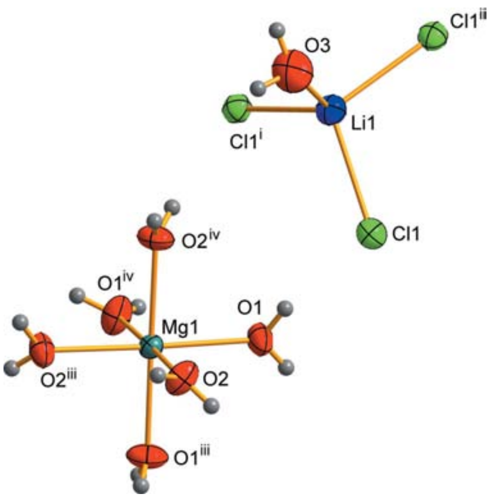

**Figure 1**
The asymmetric unit and symmetry-related atoms of $LiCl\cdot MgCl_2\cdot 7H_2O$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not labeled. [Symmetry codes: (i) $-y, x - y, z$; (ii) $-x + y, -x, z$; (iii) $-y + 1, x - y + 1, z$; (iv) $-x + y, -x + 1, z$.]

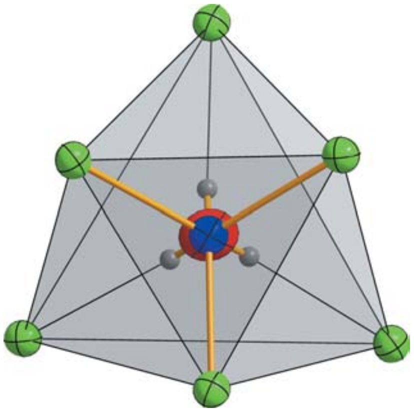

**Figure 2**
The octahedral coordination of the $Li(H_2O)^+$ unit by $Cl^-$ atoms. Each H atom shown is $\frac{2}{3}$ occupied, so only two H···Cl hydrogen bonds are present.

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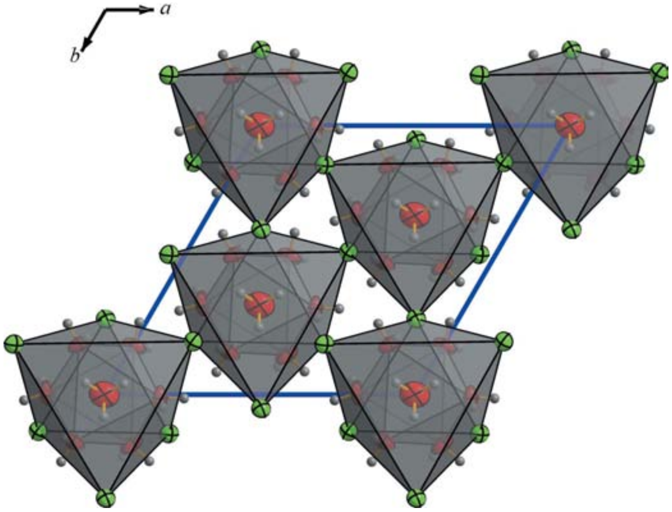

**Figure 3**
A projection along the [001] direction of a trigonal unit cell of $LiCl{\cdot}MgCl_2{\cdot}7H_2O$.

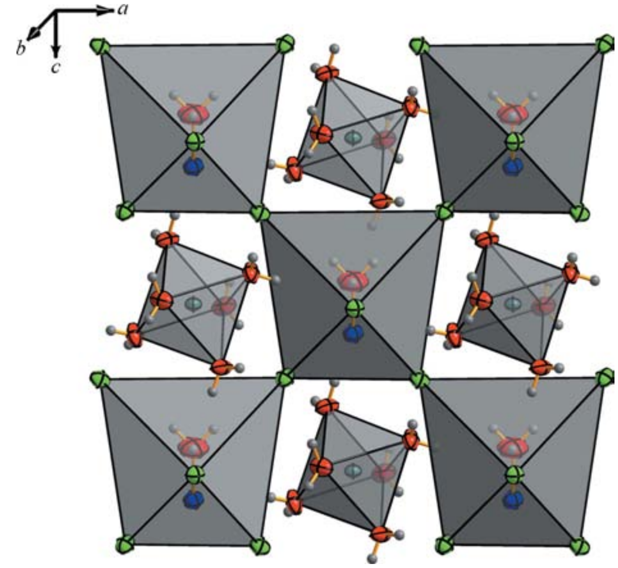

**Figure 4**
A projection showing the rhombohedral and nearly cubic framework of the lithium carnallite structure.

is stabilized by $Mg(H_2O)_6$ octahedra, which are connected to Cl atoms by $H{\cdots}Cl$ hydrogen bonds of length 2.38 (2)–2.46 (3) Å. For an insight into the contribution of hydrogen bonding in the structure, a table of $H{\cdots}Cl$ bonding parameters is given in Table 1. Four hydrogen bonds define an approximate square plane around Cl1, with the $O3—H5{\cdots}Cl1$ hydrogen bond almost perpendicular to this plane. Cl1 is slightly displaced from the plane, in the opposite direction to H5. A main reason for the trigonal lattice, as shown for the unit cell in Fig. 3, can be seen in the pseudo-trigonal symmetry of the $Li(H_2O)$ dumbbell (Fig. 2). The trigonal symmetry of the $Li(H_2O)$ unit is only a statistical average. Assuming two fixed positions for the H atoms at O3 would lower the symmetry of the crystal structure. Despite its trigonal structure, $LiCl{\cdot}MgCl_2{\cdot}7H_2O$ is structurally related to a cubic lattice. In the rhombohedral setting of the unit cell, the lattice parameters are $a = 6.675$ Å and $\alpha = 87.51°$. This nearly cubic atomic arrangement is obvious from Fig. 4.

## Experimental

$LiCl{\cdot}MgCl_2{\cdot}7H_2O$ was prepared by cooling a solution of $MgCl_2{\cdot}6H_2O$ (23.4 g) and LiCl (14.9 g) in deionized water (17.6 g) from 345 to 303 K over a period of 3 d. This was carried out in closed test tubes with constant rotation of the bubbler in a climatic chamber (Vötsch VC4043). To prevent contact of the air humidity with the crystals they were covered with *n*-hexane. A crystal of dimensions 0.3 × 0.3 × 0.3 mm was selected and embedded in a two-compound adhesive-based epoxy resin (UHU plus sofortfest) before being mounted on the single-crystal diffractometer.

### *Crystal data*

$LiCl{\cdot}MgCl_2{\cdot}7H_2O$
$M_r = 263.71$
Trigonal, $R3$
$a = 9.2322$ (3) Å
$c = 12.0541$ (5) Å
$V = 889.77$ (6) Å$^3$
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 0.82$ mm$^{-1}$
$T = 293$ K
0.30 × 0.30 × 0.30 mm

### *Data collection*

Bruker X8 Kappa diffractometer
4767 measured reflections
1150 independent reflections
1134 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

### *Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.038$
$S = 1.05$
1150 reflections
58 parameters
1 restraint
All H-atom parameters refined
$\Delta\rho_{\rm max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.20$ e Å$^{-3}$
Absolute structure: Flack (1983), 578 Friedel pairs
Flack parameter: 0.01 (4)

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

| $D—H{\cdots}A$ | $D—H$ | $H{\cdots}A$ | $D{\cdots}A$ | $D—H{\cdots}A$ |
|---|---|---|---|---|
| $O1—H1{\cdots}Cl1^{i}$ | 0.77 (3) | 2.46 (3) | 3.2156 (10) | 171 (2) |
| $O1—H2{\cdots}Cl1$ | 0.82 (2) | 2.40 (2) | 3.2056 (9) | 168 (3) |
| $O2—H3{\cdots}Cl1^{ii}$ | 0.76 (2) | 2.43 (2) | 3.1803 (11) | 172.2 (17) |
| $O2—H4{\cdots}Cl1^{iii}$ | 0.803 (19) | 2.382 (19) | 3.1845 (8) | 179 (2) |
| $O3—H5{\cdots}Cl1^{iv}$ | 0.87 (4) | 2.53 (4) | 3.3631 (7) | 160 (4) |

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

A structure solution using direct methods and a refinement of the atomic positions with respect to the isotropic displacement parameters led to the positions of the Mg, O and Cl atoms. The positions of the H and Li atoms could be located from residual electron-density maxima after further refinement. The site occupancy of the H atom belonging to O3 (Fig. 1) refined to a value of $\frac{2}{3}$, indicating that two H atoms share three equivalent positions.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; 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, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3030). Services for accessing these data are described at the back of the journal.

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