The Crystal Structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$, Containing a Magnesium-based Hetero-polycation

Robert E. Dinnebier and Martin Jansen

Max-Planck Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Reprint requests to Prof. Dr. R. Dinnebier. Fax: +49-(0)711-6891139.
E-mail: r.dinnebier@fkf.mpg.de

Z. Naturforsch. **2008**, *63b,* 1347 – 1351; received September 12, 2008

The crystal structure of di-magnesium hexahydrate trihydrogencarbonate chloride, $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$, has been determined from high-resolution laboratory powder diffraction data (lattice parameters at r. t.: a = 8.22215(2), c = 39.5044(2) Å, V = 2312.85(2) Å^3, space group $R\bar{3}c$, Z = 6). The crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ is built up of alternating sheets of Cl^- anions and complex $[Mg_2(H_2O)_6(HCO_3)_3]^+$ cations consisting of two $Mg(OH_2)_3O_3$ octahedra interconnected by three disordered hydrogen carbonate groups. The packing can be described as a cubic close packing of $[Mg_2(H_2O)_6(HCO_3)_3]^+$ cations with the Cl^- anions filling all octahedral voids. In the temperature range from r. t. up to decomposition, which takes place in the range 398 K $< T <$ 413 K, no structural phase transition occurs.

Key words: Powder Diffraction, Hetero-polycation, Magnesium Chloride Carbonate Hydrate

Introduction

The quaternary system $Mg(OH)_2$-$MgCl_2$-$MgCO_3$-H_2O contains a variety of technologically important phases. In particular the binary components magnesium carbonate $MgCO_3$ (*magnesite*) [1] and magnesium hydroxide $Mg(OH)_2$ (*brucite*) [2] are well investigated. While *magnesite* is mainly used to produce magnesium metal and basic refractory bricks, as a drying agent for hands in rock climbing, gymnastics, and weight lifting, as well as in flooring, fireproofing, fire extinguishing compositions, cosmetics, dusting powder, and toothpaste, *brucite* has applications as a fire retardant, an antacid to neutralize stomach acid, a laxative, a non antiperspirant armpit deodorant, and is used in bleaching solutions to whiten clothes and as a non-hazardous alkali to neutralize acidic wastewaters.

Several hydrated forms of *magnesite* exist as minerals, like the di-, tri-, and pentahydrates known as *barringtonite* ($MgCO_3 \cdot 2H_2O$) [3], *nesquehonite* ($MgCO_3 \cdot 3H_2O$) [4], and *lansfordite* ($MgCO_3 \cdot 5H_2O$) [5], respectively. Some basic forms such as *artinite* ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) [6], *hydromagnestite* ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) [7], *dypingite* ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$) [8], *giorgiosite* ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) [9], and *pokrovskite* ($Mg_2(CO_3)(OH)_2 \cdot 0.5H_2O$) [10] occur as minerals.

If $Mg(OH)_2$, $MgCl_2$ and water are mixed, the high quality Sorel cements are formed with many applications in industrial flooring [11]. In the ternary phase diagram of magnesium oxychlorides, four compounds have been identified so far, which are defined by the number of $Mg(OH)_2$ in their formulas: $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ (F2-phase); $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (F3-phase) [12], $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (F5-phase) [13], and $9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (F9-phase). Among these four phases, only the F3 and the F5 representatives are stable at r. t. and constitute the major binder phases in Sorel cements [14].

Some of these materials react with carbon dioxide in air forming magnesium oxychlorocarbonates. The only confirmed compound so far is *chlorartinite* which is of key importance for the quality of Sorel cements and occurs when the wet F3 phase is exposed to air. The timescale of the binding reactions spans from seconds to years. *Chlorartinite* also occurs as a volcanic exhalation product in Kamchatka, and its crystal structure was recently solved from high-resolution powder diffraction data [15, 16]. *Chloratinite* forms a zeolite-like honeycomb framework structure.

A second magnesium chloride carbonate hydrate compound with unknown crystal structure was reported by Schmittler [17] with the possible formula $Mg_2Cl_2CO_3 \cdot 7H_2O$. It can be expected that many more

0932–0776 / 08 / 1200–1347 $ 06.00

phases exist in this quaternary system with interesting crystal structures and properties. In the course of a further examination of this system, we have synthesized the new ionic compound $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$. Since single crystals of sufficient size and quality for single crystal diffraction could not be obtained, the determination of the crystal structure was performed by means of high-resolution laboratory X-ray powder diffraction.

Experimental Section

Synthesis

At adding 7.5 mL of dest. H_2O to a mixture of 20.2 mg $MgCl_2{\cdot}6H_2O$ and 17.4 mg $Mg(OH)_2$, a white suspension formed. The slurry was sealed in a glass ampoule and kept for 1 month at r. t. After heating to 100 °C for 24 h, the ampoule was opened and kept under atmospheric conditions until a white residue remained. The product was filtered off and placed for 12 h at slightly reduced pressure in an exsiccator, where it showed no noticeable change in consistency. The sample was then kept at 35 °C for one week. For filling capillaries for X-ray diffraction, the waxy sample was levigated with glass powder.

Laboratory powder diffraction

High-resolution X-ray powder diffraction patterns of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ were recorded at different temperatures on a powder diffractometer (D-8, Bruker-AXS, Cu$K_{\alpha1}$ radiation from a primary Ge(111) Johanson-type monochromator; Våntag-1 position sensitve detector (PSD) with an opening angle of 6° in Debye-Scherrer geometry) with the sample sealed in a borosilicate glass capillary of 0.5 mm diameter (Hilgenberg glass no. 50). For the measurements at elevated temperature, a water-cooled capillary heating stage (mri Physikalische Geräte GmbH) with a temperature stability ≤ 1 K was used. All samples were spun during measurement for better particle statistics. At r. t., data of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ were taken in steps of $2\theta = 0.009°$ from $2\theta = 2.0-92.0°$ at a scanning speed of $0.05° \text{ min}^{-1}$. In the range $323 \leq T \leq 533$ K, data for $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ were taken in increments of 15 K with a step width of $2\theta = 0.009°$ from $2\theta = 4.0-64.0°$ for 3 h each. For structure determination and refinement, the program TOPAS 4.0 (Bruker AXS) was used.

Indexing of the diffraction data collected at $T = 298$ K was performed by iterative use of singular value decomposition (LSI) as implemented in the program TOPAS [18], leading to a rhombohedral unit cell with lattice parameters $a = 8.22214(3)$, and $c = 39.5044(2)$ Å. The most probable space groups could be determined as $R3c$ (no. 161), or $R\bar{3}c$ (no. 167) from the observed extinction rules of which the latter could subsequently be confirmed by successful Rietveld refinements [19]. From volume increments Z was determined as 6.

Table 1. Crystallographic data for $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl$ at 298 K.

Compound	$[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$
Temperature, K	298
Formula weight, g mol^{-1}	375.21
Space group	$R\bar{3}c$ (no. 167)
Z	6
a, Å	8.22214(3)
c, Å	39.5044(2)
V, Å^3	2312.84(2)
μ(Cu$K_{\alpha1}$), cm^{-1}	37.8
ρ_{calc}, g cm^{-3}	1.61
λ, Å	1.54059
R_p[a], %	2.94
R_{wp}[a], %	3.88
R_{F^2}[a], %	2.71
Starting angle 2θ, deg	2
Final angle 2θ, deg	92
Step width 2θ, deg	0.009
Time/scan, hrs.	24
No. of variables	48
No. of reflections	225

[a] R_p, R_{wp}, and R_{F^2} as defined in TOPAS (Bruker AXS).

The peak profiles and precise lattice parameters were determined by a LeBail fit [20] using the fundamental parameter (FP) approach of TOPAS [21]. Due to the fact that the geometry of the Våntag-1 PSD is not fully characterized by FP's, fine tuning of the available parameters was performed by using refined values of the FPs from a precise measurement of the NIST line profile standard SRM 660a (LaB_6) in a 0.1 mm capillary over the full 2θ range of the diffractometer. The refinements converged quickly.

No related crystal structure could be found in the ICSD database (FIZ Karlsruhe). Therefore, structure determination was performed in space group $R\bar{3}c$ by the global optimization method of simulated annealing (SA) as implemented in TOPAS [22]. Since the exact number of atoms was not known *a priori*, 2 magnesium atoms, 2 chlorine atoms and 6 oxygen atoms with a merging radius of 0.6 Å for each kind of atoms were introduced to the simulated annealing run. After several runs, a meaningful crystal structure was found. As main structural motif, groups of two MgO_6 octahedra facing each other were identified with additional electron density between the octahedra, completing triangles of oxygen atoms with a central atom of lower scattering power, thus suggesting the existence of CO_3 groups as linking elements. Consecutive Rietveld refinements confirmed this idea and revealed the presence of disorder for the CO_3 groups in a sense that the two oxygen atoms connecting to the two MgO_6 octahedra have the function of the hinges of a swinging door, leaving the third unconnected oxygen atom with a large displacement parameter in the direction of the swing. Thus, the introduction of a slack soft constraint for that particular C–O bond

Table 2. Atomic coordinates for $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl$ at 298 K.

Atom	Wyckoff	x/a	y/b	z/c	u (Å^2)
Mg1	12*c*	0	0	0.8013(1)	0.0230(5)
Cl1	6*b*	0	0	0	0.0311(6)
C1	18*e*	0	0.3119(2)	3/4	0.0310(4)
O6	18*e*	0	0.5157(2)	1/4	[a]
O2	36*f*	0.3676(2)	−0.5348(1)	0.9435(1)	0.0310(4)
O3	36*f*	−0.1489(1)	0.5595(1)	−0.0012(1)	0.0310(4)

[a] u_{11} = 0.235(4); u_{22} = 0.000(4); u_{33} = 0.263(4 ; $u_{12} = \frac{1}{2}u_{22}$; u_{13} = −0.023(2); u_{23} = 0.

Table 3. Selected bond lengths (Å) and angles (deg) for $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl$ at 298 K.

Bond	Distance	Angle
Mg–O(2)	2.054(2) (3×)	84.91(5) – 99.77(5)
–O(3)	2.159(1) (3×)	170.35(4)
Mg–C (shortest)	3.268(2)	–
Cl–O (shortest)	3.192(2)	–
C–O(2)	1.332(1) (2×)	109.7(1) – 125.2(1)
–O(6)	1.417(2)	
O–O (shortest intermolecular distance)	2.834(2)	–

length appeared reasonable. The high quality of the Rietveld refinement (Fig. 1) allowed the correct assignment of OH and H_2O groups. In addition, for the final Rietveld refinements, all profile and lattice parameters were released which resulted in the agreement factors (*R* values) listed in Table 1. The atomic coordinates are given in Table 2, and a selection of intra- and intermolecular distances and angles is given in Table 3.

Crystallographic coordinates of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ at T = 298 K can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, (fax: (+49)7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-419878.

Results and Discussion

The crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ is built of Cl^- anions and $[Mg_2(H_2O)_6(HCO_3)_3]^+$ dinuclear cations consisting of two $Mg(H_2O)_3O_3$ octahedra interconnected by three hydrogen carbonate groups (Fig. 2). If the ions are represented by their center of gravity locations, the array of the building groups can be described by a cubic close packing of $[Mg_2(H_2O)_6(HCO_3)_3]^+$ cations, with a hexagonal c/a ratio of 1.60 and the chloride anions filling all octahedral voids (Fig. 3). Therefore, the crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ can be regarded a layer type of structure with alternating layers of anions and cations.

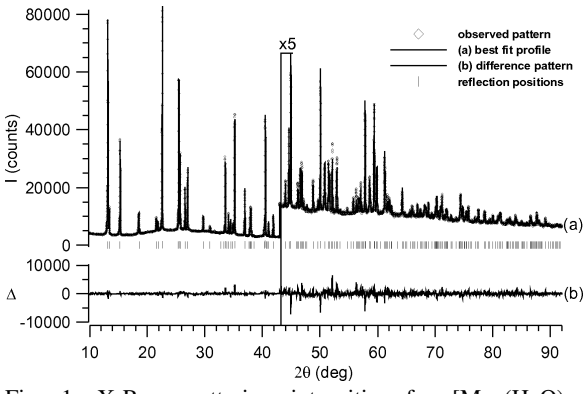

Fig. 1. X-Ray scattering intensities for $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ at T = 298 K as a function of diffraction angle 2θ (λ = 1.54059 Å), showing the observed pattern (diamonds), the calculated profile (line a), the difference plot (line b) and the reflection markers (vertical bars). Above 2θ = 43° the plot is enlarged by a factor of 5.

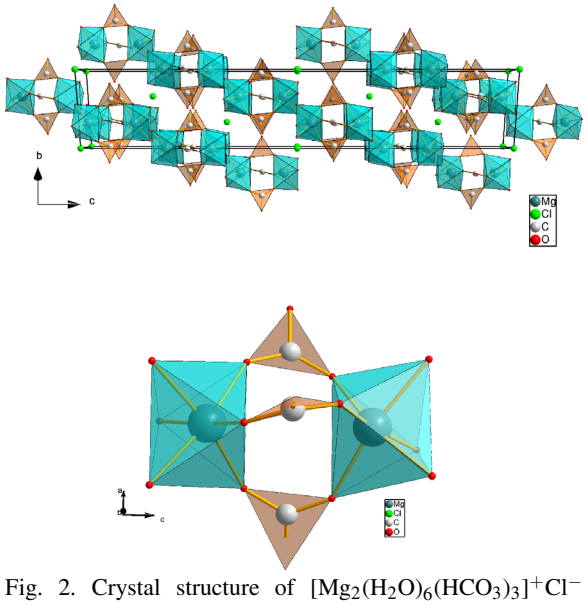

Fig. 2. Crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ at 298 K showing the packing of the building units perpendicular to the *a* axis (top) and an isolated $[Mg_2(H_2O)_6(HCO_3)_3]^+$ cation (bottom).

The hydrogencarbonate groups of $[Mg_2(H_2O)_6(HCO_3)_3]^+$ interconnecting the two $Mg(OH_2)_3O_3$ octahedra behave like "swinging doors" with the interconnecting oxygen atoms fixed in place while the non coordinating OH group is disordered. The planar carbonate groups are inclined by 12.5° with respect to the *ab* plane, explaining the strong anisotropic displacement parameters for the "free" OH group (Tab. 2, Fig. 2). Lowering the space group symmetry from $R\bar{3}c$

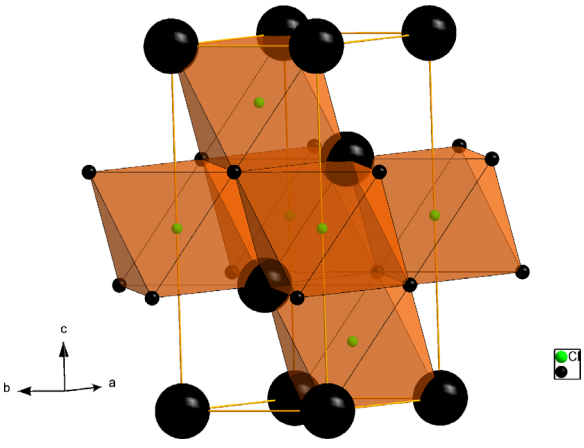

Fig. 3. Center of gravity representation of the ionic crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ at 298 K exhibiting an *fcc* type of packing.

down to *R*3*c*, in order to decrease the apparent disorder, did not reduce the displacement parameter of the "free" OH group significantly.

The crystal structure is further stabilized by hydrogen bonds between the water molecules of the $Mg(H_2O)_3O_3$ octahedra and the two oxygen atoms of the HCO_3 groups of neighboring complexes (O···O distance of 2.83 Å).

Interestingly, the packing of the building units in the crystal structure of $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$ is entirely different from that of the only other known crystal structure of a magnesium chloride carbonate hydrate – *chlorartinite* [15, 16]. *Chlorartinite* also consists of MgO_6 octahedra which are interconnected by CO_3 triangular moieties, but in contrast to $[Mg_2(H_2O)_6(HCO_3)_3]^+Cl^-$, 15-membered puckered rings are formed which are stacked to a honeycomb-like three-dimensional framework structure with large isolated channels, in which free chloride anions and disordered water molecules are trapped.

Linking of MgO_6 octahedra by carbonate or hydrogencarbonate groups can be considered a general building principle for all members of the magnesium carbonate family. Depending on the number of water molecules, and hydroxy-, and carbonate groups available, different representations of this principle are realized. The framework structure of *nequehonite* [4] is built up of infinite zigzag chains of corner-sharing MgO_6 octahedra along the *b* axis with the carbonate groups linking three MgO_6 octahedra within a chain by two common corners and one edge. Likewise, *pokrovskite* [10] forms a framework structure in a way that all carbonate groups interconnect three different double chains of distorted MgO_6 octahedra. In contrast, *artinite* [6] consists of isolated double chains of MgO_6 octahedra with the carbonate groups and water molecules pointing away from the chains. The structure is held together by hydrogen bonds only. In the crystal structure of *hydromagnesite* [7], even four MgO_6 octahedra are interconnected by a given carbonate group.

With the title compound, a new representative of this versatile class of materials has been characterized, and it can be expected that even small other variations in the chemical composition will lead to a variety of new compounds with interesting crystal structures.

Acknowledgements

The authors are grateful for the generous financial support provided by the Bundesministerium für Bildung und Forschung (BMBF) and the Fonds der Chemischen Industrie (FCI). Special thanks go to Alexandra Müller (MPI-FKF) for the preparation of the title compound.

[1] K. D. Oh, H. Morikawa, S. I. Iwai, H. Aoki, *Am. Mineral.* **1973**, *58*, 1029.
[2] G. Aminoff, *Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie* **1921**, *56*, 505.
[3] B. Nashar, *Mineral. Mag.* **1965**, *34*, 370.
[4] G. W. Stephan, C. H. MacGillavry, *Acta Crystallogr.* **1972**, *B28*, 1031.
[5] B.-N. Liu, X.-T. Zhou, X.-S. Cui, J.-G. Tang, *Science in China* **1990**, *Serie B 33*, 1350.
[6] M. Akao, S. I. Iwai, *Acta Crystallogr.* **1977**, *B33*, 1273.
[7] M. Akao, S. I. Iwai, *Acta Crystallogr.* **1977**, *B33*, 3951.
[8] G. Raade, *Am. Mineral.* **1970**, *55*, 1457.
[9] B. Friedel, *Neues Jahrb. Mineral., Monatsh.* **1975**, 196.
[10] N. Perchiazzi, S. Merlino, *Eur. J. Mineral.* **2006**, *18*, 7878.
[11] S. Sorel, *Compt. Rend.* **1867**, *65*, 102.
[12] P. M. De Wolff, L. Walter-Lévy, *Acta Crystallogr.* **1953**, *6*, 40.
[13] K. Sugimoto, R. E. Dinnebier, T. Schlecht, *Acta Crystallogr.* **2007**, *B63*, 805.
[14] H. Bilinski, B. Matkovic, C. Mazuranic, T. B. Zunic, *J. Am. Ceram. Soc.* **1984**, *67*, 266.

[15] K. Sugimoto, R. E. Dinnebier, T. Schlecht, *J. Appl. Crystallogr*. **2006**, *39*, 739.
[16] K. Sugimoto, R. E. Dinnebier, T. Schlecht, *Powder Diffr*. **2007**, *22(1)*, 64.
[17] Schmittler, *private communication* **1968**, ICDD #00-021-1254.
[18] A. A. Coelho, *J. Appl. Crystallogr*. **2003**, *36*, 86.
[19] H. M. Rietveld, *J. Appl. Crystallogr*. **1969**, *2*, 65.
[20] A. LeBail, H. Duroy, J. L. Fourquet, *Mat. Res. Bull*. **1988**, *23*, 447.
[21] R. W. Cheary, A. A. Coelho, J. P. Cline, *J. Res. Natl. Inst. Stand. Technol*. **2004**, *109*, 1.
[22] A. A. Coelho, *J. Appl. Crystallogr*. **2000**, *33*, 899.