

Orientalional disorder of $[\text{Mg}(\text{H}_2\text{O})_6]$ octahedra in the novel magnesium selenite hydrate $\text{Mg}(\text{SeO}_3) \cdot 7.5\text{H}_2\text{O}$

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The crystal structure of magnesium selenite 7.5-hydrate, $\text{Mg}(\text{SeO}_3) \cdot 7.5\text{H}_2\text{O}$ (space group $P6_3/mmc$), is characterized by two crystallographically distinct $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra, one of which is disordered over two different orientations. The selenite groups and water molecules (with partially disordered H atoms) bridge the octahedra *via* hydrogen bonds. All the atoms are located on special positions, except for one water molecule.

Comment

In the course of our studies of kroenkite-like compounds (Fleck & Kolitsch, 2003; Kolitsch & Fleck, 2006) and Tutton's salts (Fleck & Kolitsch, 2002*a,b*), we have investigated the system Rb–Mg–selenic acid. Instead of the expected binary selenate compounds, the syntheses yielded small white crystals which turned out to be a novel Mg selenite hydrate species, namely $\text{Mg}(\text{SeO}_3) \cdot 7.5\text{H}_2\text{O}$. A search of the literature showed that a total number of six Mg selenite and hydrogenselenite structures have been published (Table 3). However, we found no indication that the present compound has been encountered before. Nevertheless, this structure is remarkable because it is unique in several ways among Mg selenite and hydrogenselenite compounds.

The principal building units of the structure (Figs. 1 and 2, and Tables 1 and 2) are two crystallographically distinct $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra, both of which are located on special positions. Although both octahedra are virtually undistorted, they show significant differences. The Mg1 atoms are located at Wyckoff position $2a$ and the O1 atoms at the $12k$ positions, thus building nearly perfect octahedra. The Mg2 atoms, however, are located at the $2d$ position with the coordinating O2 atoms on the $24l$ positions. Because of the site symmetry, there are 12 symmetry-related O atoms around the Mg2 atoms, which is chemically impossible. However, the refinement indicated that this position is only half-occupied, which means that there are two possible orientations of the Mg2 octahedra in the crystal structure. The refinement gave an

occupation of 0.513 (6) for atom O2, which was then fixed with an occupancy of 0.5, as were atoms H2A and H2B. The selenite groups (on threefold axes) and two crystallographically distinct water molecules are located in the interstices between the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra. The O atoms of these water molecules are also located on special positions,

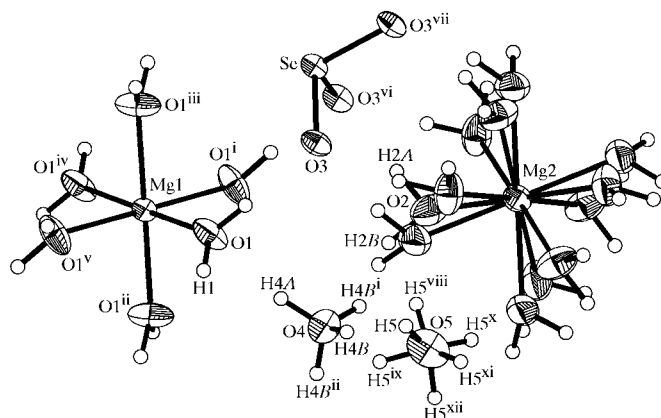


Figure 1

The connectivity in the title compound, with displacement ellipsoids at the 50% probability level. For clarity, the symmetry-equivalent O2 and H atoms of the water molecules around the Mg atoms are not labelled. [Symmetry codes: (i) $-x + y, -x, z$; (ii) $-y, x - y, z$; (iii) $y, x, -z$; (iv) $x - y, -y, -z$; (v) $-x, -x - y, -z$; (vi) $-y + 1, x - y, z$; (vii) $-x + y + 1, -x + 1, z$; (viii) $-x + y, -x + 1, z$; (ix) $-y + 1, x - y + 1, z$; (x) $x, x - y + 1, -z + \frac{1}{2}$; (xi) $-x + y, y, -z + \frac{1}{2}$; (xii) $-y + 1, -x + 1, -z + \frac{1}{2}$.]

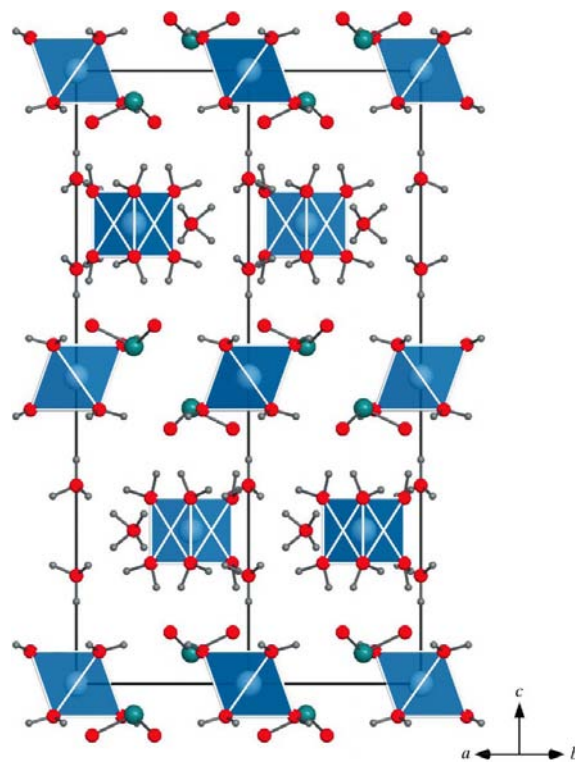


Figure 2

The packing of the structure of the title compound, viewed along $[110]$. Note the two different $[\text{Mg}(\text{H}_2\text{O})_6]$ octahedra, one of which is shown disordered between two positions at $z = \pm\frac{1}{4}$.

viz. 4*e* for O4 and 2*c* for O5. The H atoms of these molecules could be found in a difference Fourier map in partially occupied positions. Atom O4 is surrounded by four possible H-atom positions and atom O5 by six. Around O4, one H atom is located on position 4*e*, which is fully occupied. Three more symmetry-equivalent H atoms are on position 12*k*. For chemical reasons, the occupancies of these H-atom positions were fixed at 0.33. The O5 position 2*c* is surrounded by six symmetry-equivalent H atoms on position 12*k*, all of which were also assumed to be one-third occupied.

Although the refinement of hydrogen site occupancies is something to be considered with great doubt, it was attempted in this case. Most surprisingly, the refined values matched reasonably well with the assumed values for all H atoms. Of course, the refined H-atom occupancies can only be taken as an indication that the model seems to be correct. Thus, the ideal formula of the new selenite is given as Mg(SeO₃)·7.5H₂O.

Naturally, the presence of disorder in the structure may lead to the conclusion that the symmetry of the crystal was chosen incorrectly. Therefore, the refinement of structure models with lower symmetry (*P* $\bar{3}$ 1*c*, *P*31*c* and *P*3) was attempted. However, the disordered Mg2 octahedra were found in all space groups, with a refined occupancy for the O2 position of about 50%. Also, the O atoms of the non-coordinating water molecules were found to have the same occupancy as in the *P*6₃/*mmc* model. Furthermore, the lower the symmetry, the harder the refinement of the H atoms. In all cases, the final *R* indices were worse than in the *P*6₃/*mmc* case, *viz.* 0.0303, 0.0328 and 0.0342 for the space groups *P* $\bar{3}$ 1*c*, *P*31*c* and *P*3, respectively. Finally, all these structure models were checked with the program *PLATON* (Spek, 2000), which detected higher symmetry corresponding to *P*6₃/*mmc* in all cases. All these points lead to the conclusion that the higher symmetry is correct.

The presence of disordered [Mg(H₂O)₆]²⁺ octahedra in Mg(SeO₃)·7.5H₂O is unique among all the known Mg selenites and hydrogenselenites (see Table 3). The only member of this group where disorder occurs is Mg(HSeO₃)₂·3H₂O (Boldt *et al.*, 1999), which is also hexagonal (space group *P* $\bar{6}$ 2*c*). However, in this case, the disorder involves the hydrogenselenite groups.

Experimental

An equimolar mixture of Rb₂CO₃ (47.54 mg) and MgCO₃ (16.22 mg) was dissolved in dilute selenic acid. The solutions were evaporated slowly at a temperature of approximately 295 K over a period of several weeks. The syntheses yielded small colourless crystals of the title compound of up to 0.15 mm in size and also crystals of Rb₂CO₃.

Crystal data

Mg(SeO ₃)·7.5H ₂ O	<i>D</i> _x = 1.854 Mg m ⁻³
<i>M</i> _r = 286.39	Mo <i>K</i> α radiation
Hexagonal, <i>P</i> 6 ₃ / <i>mmc</i>	<i>μ</i> = 3.75 mm ⁻¹
<i>a</i> = 7.262 (1) Å	<i>T</i> = 293 (2) K
<i>c</i> = 22.470 (5) Å	Prism, colourless
<i>V</i> = 1026.2 (3) Å ³	0.10 × 0.06 × 0.06 mm
<i>Z</i> = 4	

Data collection

Nonius KappaCCD diffractometer	3869 measured reflections
<i>φ</i> and <i>ω</i> scans	655 independent reflections
Absorption correction: multi-scan (Otwinowski & Minor, 1997)	629 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.706, <i>T</i> _{max} = 0.807	<i>R</i> _{int} = 0.066
	<i>θ</i> _{max} = 30.5°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0164 <i>P</i>) ² + 0.425 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.023	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.053	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.21	Δ <i>ρ</i> _{max} = 0.48 e Å ⁻³
655 reflections	Δ <i>ρ</i> _{min} = -0.50 e Å ⁻³
55 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.044 (2)

Table 1

Selected bond lengths (Å).

Mg1—O1	2.0528 (16)	Se—O3	1.6995 (13)
Mg2—O2	2.081 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3 ^{viii}	0.95 (2)	1.76 (2)	2.6923 (12)	167 (3)
O2—H2A...O3 ^{vi}	0.948 (19)	1.77 (3)	2.671 (3)	158 (5)
O2—H2B...O4	0.95 (2)	1.97 (2)	2.897 (2)	167 (6)
O4—H4A...O1	0.95 (2)	2.481 (15)	3.245 (3)	137.6 (3)
O4—H4B...O2 ^{viii}	0.94 (2)	2.31 (2)	2.897 (2)	120.3 (15)
O5—H5...O2 ^{xiv}	0.96 (2)	2.21 (3)	3.071 (3)	148 (4)

Symmetry codes: (vi) $-y + 1, x - y, z$; (viii) $-x + y, -x + 1, z$; (xiii) $x, x - y, z$; (xiv) $-x + y + 1, y + 1, z$.

Table 3

Stoichiometries, symmetries and unit-cell parameters (Å, °) of magnesium selenite and hydrogenselenite compounds.

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>α</i>	<i>β</i>	<i>γ</i>	Space group
Mg(SeO ₃) ^a	5.925	7.666	5.006	90	90	90	<i>Pnma</i>
Mg(SeO ₃)·2H ₂ O ^b	6.482	8.798	7.637	90	98.75	90	<i>P2₁/n</i>
Mg(SeO ₃)·6H ₂ O ^{cd}	8.944	8.944	8.936	90	90	120	<i>R3</i>
Mg(SeO ₃)·7.5H ₂ O ^e	7.262	7.262	22.470	90	90	90	<i>P</i> 6 ₃ / <i>mmc</i>
Mg(HSeO ₃) ₂ ^f	9.091	5.231	5.570	90	90.94	90	<i>P2₁/n</i>
Mg(HSeO ₃) ₂ ·3H ₂ O ^g	9.434	9.434	10.492	90	90	120	<i>P</i> 6 ₂ <i>c</i>
Mg(HSeO ₃) ₂ ·4H ₂ O ^{hi}	14.646	7.553	10.999	90	126.59	90	<i>C2/c</i>

References: (a) Kohn *et al.* (1976); (b) Johnston *et al.* (2001); (c) Weiss *et al.* (1966), *R3*, hexagonal cell setting; (d) Andersen *et al.* (1984), *R3*, rhombohedral cell setting; (e) this work; (f) Boldt *et al.* (1997); (g) Boldt *et al.* (1999); (h) Engelen *et al.* (1995), *C2/c* setting; (i) Micka *et al.* (1996), *I2/a* setting.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3022). Services for accessing these data are described at the back of the journal.

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