

## **Magnesium sulfate hexahydrate at 120 K**

**Andrei S. Batsanov**

---

### **Electronic paper**

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

## Magnesium sulfate hexahydrate at 120 K

Andrei S. Batsanov

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

Correspondence e-mail: a.s.batsanov@durham.ac.uk

Received 20 April 2000

Accepted 26 April 2000

Data validation number: IUC0000132

The structure of  $[\text{Mg}(\text{H}_2\text{O})_6]\text{SO}_4$  was redetermined at 120 K, confirming the hydrogen-bond pattern found at room temperature [Zalkin *et al.* (1964). *Acta Cryst.* **17**, 235–240] but showing the librational corrections of bond lengths to be unrealistic.

### Comment

The crystal structure of the title complex, (I), known in nature as the mineral hexahydrate, was determined at room temperature by Zalkin *et al.* (1964), showing small but significant distortions of octahedral coordination of the Mg atoms. To investigate this effect, we have redetermined the structure of (I) at 120 K.

The structure contains two crystallographically non-equivalent  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations, the Mg1 and Mg2 atoms occupying Wyckoff positions 4(*a*) at an inversion centre and 4(*e*) on a twofold axis, respectively. Each Mg atom has a slightly distorted octahedral coordination with six water molecules. The sulfate anion has no crystallographic symmetry. Cations and anions are linked by a three-dimensional network of hydrogen bonds, involving all H atoms. Of the 12 hydrogen bonds, 11 are accepted by the anion and one by the O8 atom of an aqua ligand.

The present study generally confirmed the structure (including the location of the H atoms) reported by Zalkin *et al.* (1964). The latter reported a tetragonal distortion of the coordination octahedron of Mg1, with distances Mg1–O5 2.046 (2), Mg–O6 2.044 (3) and Mg–O7 2.080 (2) Å. We found a much smaller and irregular distortion, with distances [corrected for libration according to Schomaker & Trueblood (1968)] of 2.041 (2), 2.055 (2) and 2.066 (2) Å, respectively. The distortion of the second cation, with a *cis* disposition of the two longer Mg–O bonds, *i.e.* Mg2–O8 and its symmetrical equivalent [2.083 (2) *versus* Mg–O9 2.054 (2) and Mg–O10 2.059 (3) Å] is confirmed in the present study. After librational correction, we found Mg2–O8 2.083 (2), Mg2–O9 2.044 (2) and Mg–O10 2.052 (2) Å. The cause of this is obvious: O8 is the only water O atom acting as an acceptor of a

hydrogen bond. On average, the Mg–O distances in the present structure are increased by the librational corrections by 0.004 Å, but still remain shorter than the distances observed at room temperature (mean 2.06 Å), which were further corrected to an average of 2.07 Å.

The S–O bond distances in the present study coincide within one s.u. with the room-temperature data, which averaged 1.473 (7) Å. Zalkin *et al.* (1964) reported that a librational correction (assuming the O atoms to ride on the S atom) gave an average S–O distance of 1.486 (4) Å, *i.e.* the thermal libration accounted for a spurious shortening of 0.013 Å. At 120 K, we observed the  $\langle U^2 \rangle$  to be approximately half that at room temperature; thus the absence of any apparent lengthening of S–O bonds is noteworthy. Although the librational correction reduced the discrepancies between S–O distances, these discrepancies do not, in fact, result from experimental error but from the fact that the O2, O3 and O4 atoms [mean S–O 1.477 (3) Å] accept three hydrogen bonds each, while O2 [S–O2 1.464 (1) Å] accepts only two.

### Experimental

Crystals were grown from a saturated aqueous solution at room temperature.

#### Crystal data

$[\text{Mg}(\text{H}_2\text{O})_6]\text{SO}_4$   
 $M_r = 228.47$   
Monoclinic,  $C2/c$   
 $a = 9.975$  (2) Å  
 $b = 7.186$  (2) Å  
 $c = 24.267$  (6) Å  
 $\beta = 98.78$  (1)°  
 $V = 1719.1$  (7) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.765$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 552 reflections  
 $\theta = 11.9$ – $25.7$ °  
 $\mu = 0.479$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
Block, colourless  
 $0.75 \times 0.40 \times 0.35$  mm

#### Data collection

SMART 1K CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  
 $T_{\min} = 0.679$ ,  $T_{\max} = 0.837$   
6251 measured reflections  
1689 independent reflections

1604 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 26.91$ °  
 $h = -12 \rightarrow 12$   
 $k = -8 \rightarrow 8$   
 $l = -29 \rightarrow 29$   
Intensity decay: none

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.078$   
 $S = 1.189$   
1689 reflections  
159 parameters  
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 3.3810P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Mg1–O5	2.0385 (15)	Mg2–O8	2.0804 (16)
Mg1–O6	2.0485 (15)	S–O2	1.4638 (14)
Mg1–O7	2.0601 (15)	S–O4	1.4735 (14)
Mg2–O9	2.0409 (16)	S–O1	1.4764 (14)
Mg2–O10	2.0491 (14)	S–O3	1.4814 (14)
O5–Mg1–O6	90.96 (7)	O6–Mg1–O7	87.95 (7)
O5–Mg1–O7	92.87 (6)	O9 <sup>l</sup> –Mg2–O9	91.88 (9)

O9—Mg2—O10 <sup>i</sup>	93.18 (7)	O9—Mg2—O8	89.22 (6)
O9—Mg2—O10	87.25 (7)	O10 <sup>i</sup> —Mg2—O8	91.67 (6)
O10 <sup>i</sup> —Mg2—O10	179.38 (10)	O10—Mg2—O8	87.89 (6)
O9 <sup>j</sup> —Mg2—O8	178.49 (7)	O8—Mg2—O8 <sup>i</sup>	89.69 (9)

Symmetry codes: (i)  $2 - x, y, \frac{1}{2} - z$ .

**Table 2**

Hydrogen-bonding 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>
O5—H1···O1	0.82 (3)	1.97 (3)	2.780 (2)	169 (3)
O5—H2···O3 <sup>i</sup>	0.78 (3)	1.98 (3)	2.741 (2)	165 (3)
O6—H3···O3 <sup>ii</sup>	0.78 (3)	1.94 (4)	2.720 (2)	178 (3)
O6—H4···O4	0.83 (3)	1.95 (3)	2.775 (2)	169 (3)
O7—H5···O4 <sup>i</sup>	0.79 (3)	2.06 (3)	2.839 (2)	168 (3)
O7—H6···O3 <sup>iii</sup>	0.80 (4)	2.09 (4)	2.874 (2)	165 (4)
O8—H7···O1 <sup>iv</sup>	0.77 (3)	2.02 (3)	2.771 (2)	162 (3)
O8—H8···O2 <sup>v</sup>	0.82 (3)	1.86 (3)	2.685 (2)	174 (3)
O9—H9···O2 <sup>vi</sup>	0.79 (3)	1.94 (3)	2.725 (2)	172 (3)
O9—H10···O8 <sup>vii</sup>	0.75 (3)	2.24 (3)	2.969 (2)	162 (3)
O10—H11···O1	0.80 (3)	1.99 (3)	2.784 (2)	168 (3)
O10—H12···O4 <sup>viii</sup>	0.83 (3)	1.94 (3)	2.765 (2)	174 (3)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The author thanks Mr P. Richmond for preparing crystal samples and Professor J. A. K. Howard for helpful discussions.

## References

- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SMART* and *SAINTE*. Versions 6.01. Bruker AXS Inc., Madison, Wisconsin, USA.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Sheldrick, G. M. (1998). *SADABS*. University of Göttingen, Germany.
- Zalkin, A., Ruben, H. & Templeton, D. H. (1964). *Acta Cryst.* **17**, 235–240.