Structure of $Mg_6SO_2(OH)_{14}$ Determined by Micro Single-Crystal X-ray Diffraction

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Abstract

The structure of hexamagnesium sulfonyl tetradecahydroxide, $Mg_6SO_2(OH)_{14}$, has been determined with an extremely small single crystal (*ca* $0.5 \times 100 \times 2.5 \mu m$) using synchrotron radiation [$1.00(1)$ Å]. The crystal is orthorhombic with space group *Ccmm* (no. 63), $a = 15.895(1)$, $b = 3.105(1)$, $c = 13.367(1)$ Å, $V = 659.64(3)$ Å^3 and $Z = 2$. The final R and wR values are 0.073 and 0.083 for 105 crystallographically independent reflections. The structure consists of MO_6 octahedra and SO_4 tetrahedra. The MgO_6 octahedra share their edges to form zigzag sheets parallel to (100). The SO_4 tetrahedron shares two of the O atoms with the MgO_6 octahedra at the turning of the sheet and is statistically located with a probability of 0.5. Fine streaks observed perpendicular to the $b*$ axis on diffraction photographs indicate that the SO_4 tetrahedra are distributed at random along the a and c axes, but alternately along the b axis. All the H atoms are considered to exist in the form of OH groups.

1. Introduction

Crystals of $Mg_6SO_2(OH)_{14}$ can be obtained only in the form of extremely fine needles with rather low crystallinities. The maximum length and the volume are around $100 \mu m$ and $100 \mu m^3$, respectively. The crystal structure has remained unsolved since the crystals are too small to carry out intensity measurements with the single-crystal diffraction method and, in addition, the acicular shape of the crystals prevents the quantitative analysis of the intensities obtained with the powder diffraction method.

Recently, Ohsumi, Hagiya & Shimizugawa developed a Weissenberg camera applicable to ultramicro single crystals of dimensions even smaller than $10 \mu m$ in combination with synchrotron radiation. The camera employs an imaging plate (Fuji Film Co. Ltd) in place of X-ray films to record the X-ray diffraction patterns (Miyahara, Takahashi, Amemiya, Kamiya & Satow, 1986). The X-ray diffraction intensity measurements of the title crystal were successfully carried out with the help of this camera. The details of the camera will be described elsewhere.

2. Experimental

Colourless acicular crystals of the compound were grown from a mixture of aqueous solutions of $Mg(OH)_2$ and $MgSO_4$ in the molar ratio 2:1 under hydrothermal conditions at *ca* 450 K. The cell dimensions of the crystals were determined with the powder diffraction method by Yoshitomi (1990), utilizing specimens from the same batch as in the present study. He derived the values from diffraction data in the range $15 < 2\theta < 60°$ collected with Cu $K\alpha$ radiation (1.5418 Å) with the help of the program *WPPD* for the whole powder pattern decomposition method (Toraya, 1986). These values were adopted in the present study.

The intensity collection was carried out at station BL-4B at the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan. The synchrotron radiation beam was monochromated with an Si(111) double-crystal monochromator to obtain $1.00(1)$ Å radiation. The storage ring was operated at 2.5 GeV and a positron current of 350–200 mA. The Weissenberg camera used has a radius of 100 mm. Imaging plates of size 20×40 cm were employed to record the diffraction spots. The camera was placed in a vacuum chamber to reduce air scattering, where experiments with the Laue method have been carried out on submicrometer-sized single crystals using polychromatic synchrotron radiation (Ohsumi, Hagiya & Ohmasa, 1991). During exposure, the chamber was kept at reduced pressure (~1 Pa). Because of the branch beamline (BL-4C) that passes just beside BL-4B, the range of cassette movement in the Weissenberg mode is limited to 48 mm. However, the coupling ratio of movement and oscillation angle can be chosen arbitrarily.

Several acicular crystals with better crystallinities were selected under an optical microscope and mounted on fine glass fibres with the elongation direction of the crystals parallel to the fibre axes, by making use of a micro-manipulator. The direction of elongation was confirmed by electron microscopic observation and electron diffraction to be parallel to the b axis. Thus, the rotation axis of the X-ray photographs corresponds to the b axis in the present arrangement. First, oscillation photographs were taken with the respective specimens. All the specimens were found to give diffraction spots

markedly elongated in the directions along which powder rings are expected to appear. Accordingly, the crystals were assumed to be composed of fine needles not in exactly the same orientation. A crystal giving relatively sharp diffraction spots was chosen for intensity measurements. The X-ray photographs as well as electron diffraction photographs always gave sharp streaks perpendicular to the b^* axis, halving the b^* period. This phenomenon indicates that the crystal has a structure containing some disorder along the directions perpendicular to b.

The crystal used for intensity measurements has the dimensions *ca* $0.5 \times 100 \times 2.5 \ \mu m^3$. Weissenberg photographs were taken with the normal beam method and without using the layer-line screen to avoid the scaling of intensities of reflections on different layers and to save time for data collection.

It required 7–8 h to take a Weissenberg photograph of adequate density. Oscillation ranges were overlapped by 20 or 15° and eight photographs were taken to cover the range 195° around the oscillation axis. Intensity collection was carried out only for the −1st, 0th and 1st layers. Measurements were not made for the reflections of the 2nd layer, since the spots on this layer were largely elongated because of the lower glancing angles of the diffracted beams to the imaging plate in addition to the lower crystallinity of the specimen. In practice, the structure could be solved with data from the 0th and 1st layers, since the crystal has a short b period and a C-centred lattice. Intensity data were obtained on 417 reflections ($-14 \leq h \leq 16, -1 \leq k \leq 1, -11 \leq l \leq 14$), of which 105 were crystallographically independent. The value of R_{int} was 0.058. The observed intensities were corrected for the Lorentz and polarization factors. The polarization factors were evaluated by assuming the incident beams to be perfectly polarized in the horizontal plane that includes the positron orbit and the rotation axis of the Weissenberg camera. The linear absorption coefficient was estimated to be $1.19 \ mm^{-1}$ based on the atomic absorption coefficients given by Sasaki (1990), neglecting the contributions of H atoms. No absorption corrections were applied because of the small size of the specimen. The density of the crystals, $2.3 \ Mg \ m^{-3}$, was measured by the Archimedian method and agreed well with the calculated value of $2.26 \ Mg \ m^{-3}$.

3. Structure determination

The observed extinction rule, $h + k = 2n$ for hkl, indicates that the crystal has a C-base-centred lattice. Since only the reflection data of the 0th and 1st layers were collected around the b axis, the existence of c-glide planes perpendicular to the a axis or 2_1 screw axes parallel to c could not be clearly confirmed, although only 008 and 0,0,10 reflections were observed among the $0kl$ reflections. Therefore, the possible space groups

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

The displacement parameters are of the form $\exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$.

		x	y	z	U_{iso}
Mg(1)	4(a)	0.0	0.0	0.0	0.018 (4)
Mg(2)	8(f)	0.3748 (5)	0.0	0.1322 (6)	0.012 (3)
S	4(c)	0.1929 (12)	0.0	1/4	0.011 (5)
O(1)	4(c)	0.3887 (13)	1/2	1/4	0.012 (7)
O(2)	8(g)	0.1404 (16)	0.370 (16)	1/4	0.026 (10
O(3)	8(f)	0.0028 (10)	1/2	0.1066 (10)	0.009 (5)
O(4)	8(f)	0.1290 (9)	0.0	−0.0340 (10)	0.011 (5)
O(5)	8(f)	0.2441 (10)	0.0	0.1511 (11)	0.025 (5)

are $Cmmm$, $Ccmm$, $Cmm2$, $Cm2m$, $Cc2m$, $Ccm2_1$, $C222$ and $C222_1$.

The structure was solved by the Patterson method and refined with the full-matrix least-squares program *LINKT*80 (Tanaka & Marumo, 1983) assigning isotropic thermal parameters for all the atoms. The function minimized was $\Sigma(|F_c| - |F_c|)^2$ and unit weights were given for all reflections. H atoms were not included in the calculations even at the final stage. The space group was determined to be $Ccmm$ in the course of the structure determination within the accuracy of the present experiment. The atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion corrections were not applied. The rather high final R and wR values (0.073 and 0.083) are considered to be due first to the low accuracy of the intensity data resulting from the low crystallinity and small size of the specimen, and second to the existence of disorder in the structure. The final atomic parameters are given in Table 1.*

4. Results and discussion

Selected interatomic distances and bond angles are listed in Table 2. The atomic arrangements and the linkage of coordination polyhedra in the structure are shown in Figs. 1 and 2. The structure is based on strings of edge-sharing MgO_6 octahedra running along the b axis (the needle direction). The strings further share the edges of octahedra to form folded sheets of composition Mg_6O_{14} parallel to (100). The sheets are stacked along the a axis, accompanying relative shifts of half a period in the b direction between neighbouring layers, and supposedly combined with hydrogen bonds. The SO_4 group is bound to the sheet at its turning point by sharing two of the four O atoms with the MgO_6 octahedra; however, the S and two unshared O(2) atoms are statistically located over the crystallographically equivalent positions with occupancy factors of 50%.

Table 2. *Interatomic distances (Å) and bond angles (°)*

Mg(1) octahedron

Mg(1)—O(3) × 4	2.11 (1)	Mg(1)—O(4) × 2	2.10 (1)
O(3)—O(3^i) × 2	2.85 (3)	O(3)—O(3^{iii}) × 2	3.1047 (1)
O(3)—O(4) × 4	3.16 (2)	O(3)—O(4^i) × 4	2.78 (2)
O(3)—Mg(1)—O(3^i)	85.1 (4)	O(3)—Mg(1)—O(3^{iii})	94.9 (4)
O(3)—Mg(1)—O(4)	97.2 (5)	O(4)—Mg(1)—O(3^i)	82.8 (5)

Mg(2) octahedron

Mg(2)—O(1) × 2	2.22 (1)	Mg(2)—O(3^{vi})	2.06 (2)
Mg(2)—O(4^{iv}) × 2	2.03 (1)	Mg(2)—O(5)	2.09 (2)
O(1)—O(1^{iii})	3.1047 (1)	O(1)—O(3^{vi}) × 2	3.06 (2)
O(1)—O(4^{iv}) × 2	2.90 (2)	O(1)—O(5) × 2	3.07 (2)
O(3^{vi})—O(4^{iv}) × 2	2.78 (2)	O(4^{iv})—O(4^v)	3.1047 (1)
O(5)—O(4^{iv}) × 2	2.99 (2)		
O(1)—Mg(2)—O(1^{iii})	88.6	O(1)—Mg(2)—O(3^{vi})	91.1 (5)
O(1)—Mg(2)—O(4^{iv})	85.8 (3)	O(1)—Mg(2)—O(5)	90.7 (5)
O(3^{vi})—Mg(2)—O(4^{iv})	85.5 (6)	O(4^{iv})—Mg(2)—O(4^v)	99.5 (5)
O(5)—Mg(2)—O(4^{iv})	92.8 (6)		

S tetrahedron

S—O(2) × 2	1.42 (5)	S—O(5) × 2	1.55 (2)
O(2)—O(2^{iii})	2.30 (1)	O(2)—O(5)	2.41 (4)
O(5)—O(5^{ii})	2.64 (3)		
O(2)—S—O(2^{iii})	108 (3)	O(2)—S—O(5)	108 (2)
O(5)—S—O(5^{ii})	117 (2)		

Interlayer

O(2)—O(3)	2.94 (3)	O(4)—O(5)	3.08 (2)

Symmetry codes: (none) x, y, z; (i) $-x, y, -z$; (ii) $x, y, \frac{1}{2} - z$; (iii) $x, -y, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (vi) $\frac{1}{2} + x, -\frac{1}{2} + y, z$.

The edge formed by the unshared O atoms of the SO_4 tetrahedron is parallel to the *b* axis, while the *b* length (3.105 Å) is restricted to the edge length of the MgO_6 octahedron in this structure. Since the latter edge is much longer than the O—O distance in an SO_4 tetrahedron, but much less than double the length, the SO_4 groups cannot occupy all the symmetrically equivalent positions in a way to fit with the sheets of MgO_6 octahedra. Therefore, the SO_4 tetrahedra are obliged to locate alternately along the *b* axis. As mentioned above, the crystal gives fine streaks perpendicular to the *b** axis on diffraction photographs, halving the *b** period. This fact suggests that the SO_4 tetrahedra are distributed at random along the *a* and *c* axes, but alternately along the *b* axis.

There are two crystallographically independent MgO_6 octahedra. In $Mg(1)O_6$ the shared edges, O(3)—O(3^i) and O(3)—O(4^i), are much shorter than the unshared ones. In $Mg(2)O_6$, there are three independent shared edges, among which O(1)—O(1^{iii}) apparently has a length equal to *b* owing to the assumed symmetry. The remaining two, O(1)—O(4) and O(3)—O(4), also have shorter lengths than the unshared edges. The mean Mg—O distances are *ca* 2.11 Å in both octahedra, although differences between crystallographically independent bonds are much larger in $Mg(2)O_6$ than in $Mg(1)O_6$. The S—O(2) and S—O(5) distances corre-

spond to the S—O and S—OH distances in the H_2SO_4 structure, respectively. The O(5)—S—O(5^{ii}) angle is much larger than the tetrahedral angle owing to sharing of O(5) atoms with MgO_6 octahedra.

Three types of H atoms seem to exist. The first is assumed to form a hydrogen bond between O(4) and O(5) occupying the 8(*f*) site of the space group. The second is considered to form a hydrogen bond between O(2) and O(3), occupying the 16(*h*) site. The third is bound to O(5) in the case when there is no S atom bonded to the relevant O(5) atom. These expected hydrogen bonds are shown in Fig. 1 with dotted lines. The O(2)—O(3) (2.94 Å) and O(4)—O(5) (3.08 Å) distances are actually much shorter than the van der Waals contacts of O atoms.
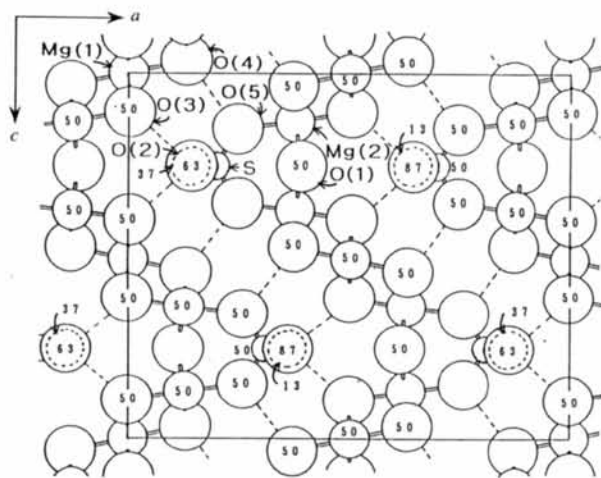

Fig. 1. The structure of $Mg_6SO_2(OH)_{14}$ viewed along the *b* axis. The numerals indicate the fractional heights multiplied by 100. The atoms without height indications are on the 0 level.
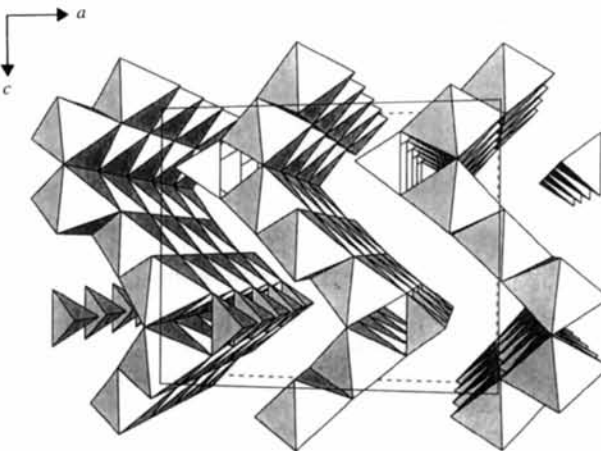

Fig. 2. A perspective drawing of the arrangement of coordination polyhedra in the structure of $Mg_6SO_2(OH)_{14}$ viewed along the *b* axis.

The most prominent face is (100) in this crystal. This feature is in accordance with the fact that the structural units are linked with rather weak hydrogen bonds along the *a* axis, whereas the units are held together by strong Mg—O bonds within the plane parallel to the *b* and *c* axes.

Although we were unable to measure the exact thickness of the crystal with an optical microscope, it is not larger than 0.5 μm. Further, it is evident that a crystal of length 100 μm is not required to measure intensities in the present case. Therefore, the device developed by Ohsumi, Hagiya & Shimizugawa can be said to have opened a way for the determination of crystal structures based on diffraction data from single crystals with sizes close to the optimum grain sizes in the powder diffraction. Based on this successful structure analysis, a newly designed Weissenberg camera has been commissioned at BL-4B.

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