April, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *57, 1155—1156 (1984)* 1155

The Crystal Structure of Calcium Sulfite Hemihydrate

Takashi Matsuno,* Hiroaki Takayanagi,† Kimio Furuhata,† Masumi Koishi,†† and Haruo Ogura†
School of Medicine, Kitasato University, Kitasato, Sagamihara 228
†*School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108*
††*Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science,*
Science University of Tokyo, Ichigaya,
Funagawaramachi, Shinjuku-ku, Tokyo 162

(Received August 3, 1983)

Synopsis. The crystal data for calcium sulfite hemihydrate are orthorhombic, Pbcn, a=10.664(1), b=6.495(1), c=9.823(1) Å, and Z=8. The structure consists of two alternating layers. The calcium ions are coordinated by six O atoms: Five originate from the sulfite ions, and one from the water molecule.

There are only two papers relating the crystal structures of calcium sulfite: One reports the cell dimensions of calcium sulfite hemihydrate crystal[1] and the other the crystal structure of calcium sulfite tetrahydrate.[2]

This study deals with the crystal structure of calcium sulfite hemihydrate obtained as a stable phase in the temperature range from 0 to 98 °C.

Experimental

Preparation. Single crystals of the hemihydrate were synthesized from calcium chloride solution(1.0 M, 1M=1 mol dm^{-3}) and sodium sulfite solution (1.0 M) by the diffusion method (25 °C, 4 weeks). Single crystals were obtained in the form of transparent plates with thicknesses of 0.1—0.4 mm. Analysis: Found: CaO, 43.3; SO_2, 49.5; H_2O, 7.1%. Calcd for $CaSO_3 \cdot 0.5H_2O$: CaO, 43.4; SO_2, 49.6; H_2O, 7.0%.

Determination of the Cell Constants and Collection of the Intensity Data. A crystal with the approximate dimension of 0.2×0.1×0.2 mm was used for the determination of cell constants and the collection of intensity data at 18 °C. The cell constants were determined by the least-squares method based on the 2θ values of 21 reflections. Crystal data: $CaSO_3 \cdot 0.5H_2O$, $F.W.$=129.1, orthorhombic, space group Pbcn, a=10.664(1), b=6.495(1), c=9.823(1) Å, V=680.4(3) Å^3, Z=8, D_c=2.521, D_m=2.51 g cm^{-3} (by flotation method). The reflection data for X-ray structural determination were collected with a Rigaku automatic four-circle diffractometer using graphitemonochromatized Cu $K\alpha$ radiation. Background was counted for 5 s at either side of each peak. The fluctuations in intensity of the three standard reflections measured every 50 reflections were about 1.1% during the data collection. Intensities of 741 independent reflections were measured up to θ=70°. Reflections having intensities stronger than four times the respective standard deviations were treated as observed. 519 non-zero reflections were obtained and corrected for Lorentz and polarization factors, but no correction was made for absorption.

Determination and Refinement of the Structure

The structure was determined by the symbolic addition method.[3] All the non-hydrogen atoms in the asymmetric unit were located from the E map. Refinement of atomic parameters was carried out by the full-matrix least-squares method, the quantity minimized being $\sum w(|F_o| - |F_c|)^2$ with w=1.0 for all the reflections. Four cycles of the least-squares refinement of the coordinates with isotropic temperature factors gave an R value of 0.082. Anisotropic temperature factors were introduced for all the atoms except hydrogen atoms, the R value being slightly reduced to 0.081. The atomic scattering factors for S and O were given by Cromer and Mann,[4] and that for Ca by International Tables for X-ray Crystallog-

Table 1. Atomic coordinates(×10^4), their estimated standard deviations(in parentheses) and equivalent isotropic temperature factors

Atom	X	Y	Z	$B_{eq}$$^{a)}$/Å^2
Ca(1)	1458(2)	5124(3)	1314(2)	1.0
S(1)	1287(2)	1690(4)	3849(3)	1.3
O(1)	526(8)	3657(13)	3985(8)	1.9
O(2)	2150(8)	1811(14)	5055(8)	2.4
O(3)	2089(8)	2095(13)	2606(8)	2.1
O(4)	0	7562(17)	2500	1.7

a) B_{eq} defined according to Hamilton(1959).[7]

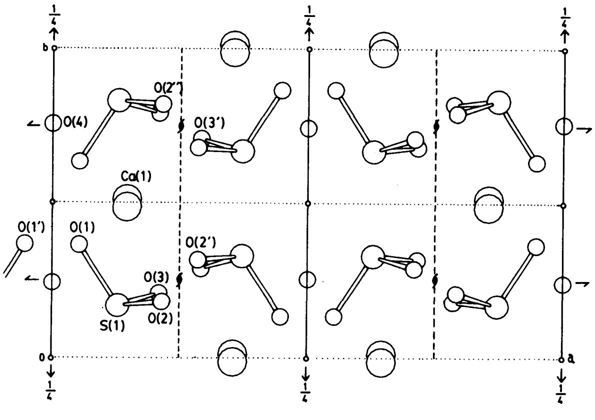

Fig. 1. Projection of the structure along the c axis and numbering of the atoms.

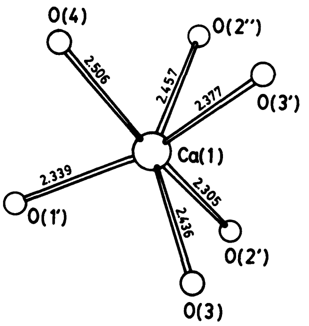

Fig. 2. Environment of the calcium ion. Interatomic distances are in Å units.

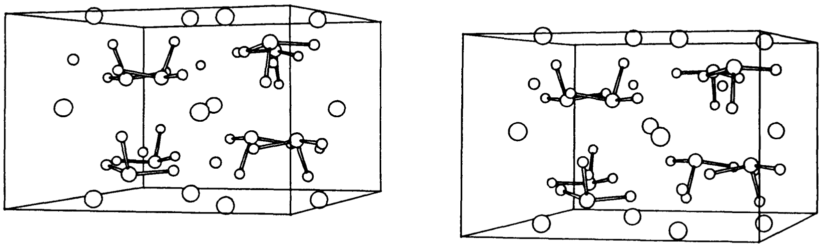

Fig. 3. Stereoscopic view of the structure.

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Interatomic	Distance l/Å	Bond angle	ϕ/°
Ca(1)-O(1')	2.339(1)	O(1')-Ca(1)-O(4)	75.79(1)
Ca(1)-O(2')	2.305(1)	O(2')-Ca(1)-O(3)	70.20(1)
Ca(1)-O(2")	2.457(1)	O(2")-Ca(1)-O(3')	68.69(1)
Ca(1)-O(3)	2.436(1)	O(1')-Ca(1)-O(3)	89.22(1)
Ca(1)-O(3')	2.377(1)	O(2')-Ca(1)-O(3')	99.23(1)
Ca(1)-O(4)	2.506(1)	O(2")-Ca(1)-O(4)	84.74(1)
Sulfite ion		O(2')-Ca(1)-O(2")	88.76(1)
S(1)-O(1)	1.519(1)	O(3)-Ca(1)-O(3')	88.67(1)
S(1)-O(2)	1.502(1)	Sulfite ion	
S(1)-O(3)	1.514(1)	O(1)-S(1)-O(2)	102.4(1)
O(1)-O(2)	2.354(1)	O(1)-S(1)-O(3)	103.1(1)
O(1)-O(3)	2.375(1)	O(2)-S(1)-O(3)	106.3(1)
O(2)-O(3)	2.414(1)		

raphy.5) The dispersion corrections for atomic scattering factors of Ca and S are 0.3 and 0.3 for $\Delta f'$ and 1.4 and 0.6 for $\Delta f''$, respectively. At the final stage of the refinement the difference Fourier map showed only featureless peaks. For these calculations, computer programs made by Stewart *et al.*6) were used. Anisotropic temperature factors of the non-hydrogen atoms and the complete F_o-F_c data are deposited as Document No. 8406 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. The final atomic coordinates, their estimated standard deviations, and equivalent isotropic temperature factors are given in Table 1.

Description and Discussion of the Structure

A projection of the structure along the c axis and the numbering of the atoms are shown in Fig. 1. The oxygen atoms O(1)-O(3) belong to the sulfite ion, and the oxygen atom O(4) belongs to the crystal water. The oxygen atoms of water molecules are situated on the twofold axes. No such sulfite ions in a disordered state as observed in the structure of calcium sulfite tetrahydrate2) exists in that of the hemihydrate crystal. The interatomic distances and angles are given in Table 2. The S-O and O-O interatomic distances and O-S-O bond angles in the $S(1)O_3^{2-}$ ion are 1.502(1)—1.519(1) Å, 2.354(1)—2.414(1) Å, and 102.4(1)—106.3(1)°, respectively. These values are similar to those (1.52(2)—1.53(3) Å, 2.37(1)—2.39(1) Å, 102.2(3)—102.9(4)°) calculated from the atomic coordinates2) of the sulfite ion in the ordered state in the structure of the tetrahydrate crystal. The coordination of O atoms around the Ca(1) ion is shown in Fig. 2. The calcium ions are coordinated by six O atoms. This number is the same as that of the Ca-coordinated O atoms in the tetrahydrate crystal.2) Five of them originate from the $S(1)O_3^{2-}$ ions(O(1'), O(2'), O(2''), O(3), O(3')), and the other from the water molecule(O(4)). The Ca(1)-O(4) distance of 2.506(1) Å is longer than the other Ca(1)-O distances(2.305(1)-2.457(1) Å). For the tetrahydrate crystal, contrary to the hemihydrate crystal, the Ca-O(sulfite ion) distances(2.52(1)-2.53(7) Å) are longer than the Ca-O (water) distances (2.38(1)-2.45(1) Å).2) The average Ca-O distance in the hemihydrate crystal (2.403 Å) is slightly shorter than 2.45 Å in the tetrahydrate crystal.

It can be presumed that the high thermostability of the hemihydrate is caused by the existence of Ca-O bondings stretched like a net all over the crystal and by the absence of the sulfite ions in a disordered state. A stereoscopic view of the crystal structure is shown in Fig. 3. The structure consists of two alternating layers similar to those in the tetrahydrate crystal: One consists of the calcium ions alone, and the other of the sulfite ions and water molecules. They are parallel to the (010) plane.

References

1) K. Setoyama, S. Takahashi, and M. Sekiya, *Gypsum Lime,* **141**, 3 (1976).

2) T. Matsuno, H. Takayanagi, K. Furuhata, M. Koishi, and H. Ogura, *Chem. Lett.,* **1983**, 459.

3) I. L. Karle and J. Karle, *Acta Crystallogr., Sect. A,* **16**, 969 (1963); **21**, 894 (1966).

4) D. Cromer and J. Mann, *Acta Crystallogr., Sect. A,* **24**, 321 (1968).

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1962), Vol. III.

6) J. M. Stewart *et al.*, Technical Report TR-192 (June, 1972), The X-Ray System of Crystallographic Programs for Any Computer, Computer Science Center, University of Maryland.

7) W. C. Hamilton, *Acta Crystallogr.,* **12**, 609 (1959).