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THE CRYSTAL STRUCTURE OF CALCIUM SULFITE TETRAHYDRATE

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The crystal structure of calcium sulfite tetrahydrate has been determined by the single-crystal X-ray diffraction method. The crystal of the tetrahydrate is monoclinic with space group C2/c, cell dimensions : a=19.385(11) Å, b=11.192(4) Å, c=11.449(10) Å, β=124.34(4)° and Z=12. The crystal structure has been determined by the symbolic addition method and refined by the full-matrix least-squares method to give the final R value of 0.084 for 1744 non-zero reflections.

It is known that only the crystals of calcium sulfite hemihydrate is produced in the reaction system of calcium hydroxide suspension and sulfur dioxide in the temperature range from 0 to 98°C.[1-4] A part of the authors(T.M. and M.K.)[5] reported that fine crystalline calcium sulfite tetrahydrate was produced below 10°C when a small amount of sodium citrate was added to the reaction system. The crystal is thermally quite unstable and separates part of the crystal water and changes to the hemihydrate quickly at room temperature and in scores of hours even at 4°C. A single crystal of the tetrahydrate large enough for structure analysis has never been obtained before, because it is stable only at low temperatures, easily twinned and has a low growth rate. The purpose of this study is to grow a large single crystal of tetrahydrate and to determine its crystal structure.

A single crystal of the tetrahydrate was synthesized by the gel method which can easily decrease the diffusion velocity of the reaction material. A u-tube of acrylic resin, 26 mm in inner diameter, was used for growing single crystals. Agar-agar was added to distilled water of 90°C up to 0.5 wt% and was completely dissolved. The sodium citrate was added to it up to 5.0×10^{-3}M. The solution was injected into the horizontal part(150 mm long) of the u-tube and was kept at 4°C for 12 h to prepare gels. Sulfurous acid solution of 0.2 M was filled up in one of the vertical parts of the tube and calcium hydroxide suspension of 0.5 M(including sodium citrate of 5.0×10^{-3}M), in another one. The tube was tightly sealed. The whole tube was immersed into water of 4°C and the temperature was kept as constant as possible. Single

crystals of the tetrahydrate of approximately 1.5 mm long were obtained in 50 days by this procedure.

The chemical composition of the tetrahydrate was CaO:29.3 wt%, SO_2:33.2 wt% and H_2O:37.2 wt%. These values agreed well with the calculated values. Characteristic absorption bands due to crystal water(3900-3000 cm^{-1}, 1630 cm^{-1}) and sulfite ion (930 cm^{-1}) were observed by infrared analysis(4000-650 cm^{-1}) of the single crystal. No other absorption bands were observed. The density of the crystal was determined to be 1.88 $g \cdot cm^{-3}$ by the flotation method.

A crystal with dimensions of 0.4x0.4x0.4 mm was used for the intensity measurement. The determination of cell constants and the intensity measurement were carried out in the temperature range from -5 to -2°C. Three dimensional intensity data were collected on a Rigaku automatic four-circle diffractometer with Cu Kα radiation monochromatized by a graphite plate. Background was counted for 5 s at either side of each peak. Three standard reflections were measured every 50 reflections. A total of 3794 independent reflections were collected. Reflections having intensities exceeding the corresponding standard deviations by a factor of four were treated as observed. 1744 non-zero reflections were obtained and corrected for Lorentz and polarization factors, but no correction was made for absorption. Crystal data are listed in Table 1.

Table 1. Crystal data

$CaSO_3 \cdot 4H_2O$	
Monoclinic	Space group C2/c
a=19.385(11) Å	V=2051(2) $Å^3$
b=11.192(4) Å	Dm=1.88 $g \cdot cm^{-3}$
c=11.449(10) Å	Dc=1.866 $g \cdot cm^{-3}$
β=124.34(4)°	Z=12

The structure was determined by the symbolic addition method.[6] 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 $\Sigma w(|F_o| - |F_c|)^2$, with w=1.0 for all the reflections. Four cycles of least-squares refinement of the coordinates with isotropic temperature factors gave an R value of 0.102. The occupancies of the disordered atoms were determined by the use of height ratios of the peaks in the Fourier map(S(2):1, O(4):1/2, O(5)-O(7):1/3). Anisotropic thermal parameters were introduced for all the atoms, the R value being reduced to 0.084. The atomic scattering factors for S and O were given by Cromer and Mann,[7] and the factor for H by Stewart et al.,[8] and that for Ca from International Tables for X-ray Crystallography.[9] The dispersion corrections were made for atomic scattering factors of Ca and S. For these calculations, computer programs made by Stewart et al.[10] were used. The final atomic coordinates(x10^4), their standard deviations(in parentheses) and equivalent isotropic temperature factors are given in Table 2.

Table 2. Atomic coordinates($\times 10^4$), their standard deviations(in parentheses) and equivalent isotropic temperature factors

Atom	x	y	z	B_{eq}(Å^2)[a]
Ca(1)	0(0)	440(2)	2500(0)	0.8
Ca(2)	1031(1)	3530(1)	2502(2)	0.7
S(1)	771(1)	2500(2)	4813(2)	0.1
S(2)	2500(0)	2500(0)	0(0)	3.0
O(1)	-81(3)	1885(5)	4112(6)	0.8
O(2)	1152(3)	1890(5)	4116(6)	0.9
O(3)	533(3)	3725(5)	4101(6)	0.8
O(4)	2002(9)	2492(15)	-1519(13)	2.7
O(5)	2334(15)	1597(19)	688(22)	6.6
O(6)	3384(11)	2376(23)	673(22)	4.5
O(7)	2501(14)	3583(18)	681(21)	5.2
O(8)	694(5)	891(7)	-540(8)	2.8
O(9)	1138(4)	288(6)	7346(7)	1.9
O(10)	745(4)	4321(6)	7336(7)	1.9
O(11)	1056(5)	4126(7)	534(8)	3.9
O(12)	2042(4)	2114(6)	2653(7)	1.9
O(13)	2674(4)	749(6)	5529(8)	1.2

a) B_{eq} defined according to Hamilton(1952)[11]

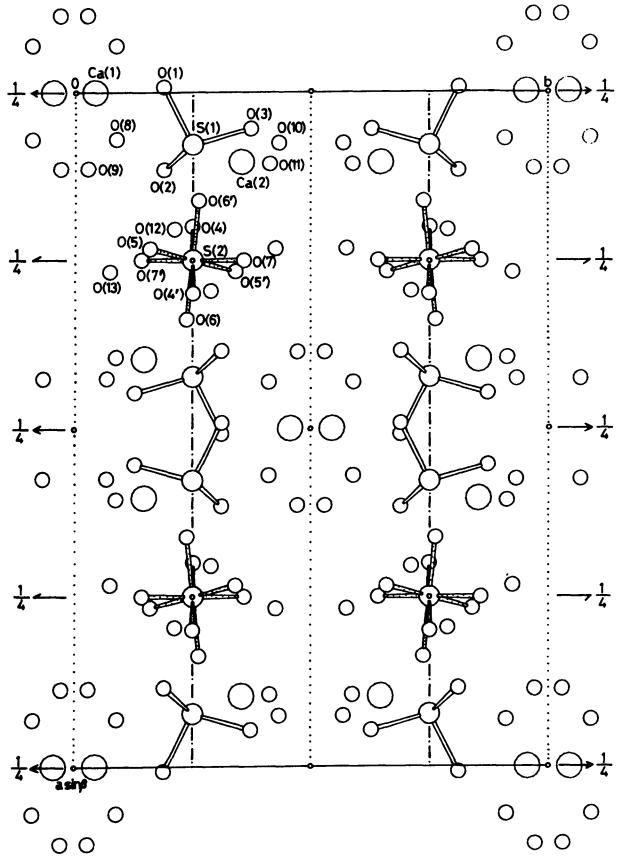

Fig. 1. Crystal structure viewed along the c axis

The crystal structure viewed along the c axis and numbering are shown in Fig. 1. The oxygen atoms O(1)-O(7) belong to sulfite ions, and the oxygen atoms O(8)-O(13) belong to the crystal water. The four oxygen atoms O(4) (O(4')), O(5)(O(5')), O(6)(O(6')), and O(7)(O(7')) are situated in the positions which permit the σ-bondings with the sulfur atom S(2). The configurations of these atoms resemble those in SO_4^{2-} ion. But the existence of SO_4^{2-} ion was negated by chemical analysis and infrared analysis. This fact may be explained as follows : a disorder in orientation occurs as illustrated in Fig. 2. The values of equivalent isotropic temperature factors for the atoms in $S(2)O_3^{2-}$ ion are larger than those in $S(1)O_3^{2-}$ ion. It can therefore be presumed that $S(2)O_3^{2-}$ ion as a whole is in a disordered state. Such disordered-structures can be observed in ClO_4^- ion and so forth.[12]

The sulfur atom S(2) is situated in the position of the center of symmetry. It is apparent that all the SO_3^{2-} ions are aligned in parallel to a axis(Fig. 1). Ca(1) and Ca(2) are coordinated by six O atoms : four originate from the water molecules, and the others are from S(1)O_3^{2-} ion, respectively. The geometries of the Ca(1)-coordinated O atoms are comparable to those of Ca(2)-coordinated O atoms. Thus, the averages of the Ca-O bond lengths are almost exactly the same(Ca(1)-O:2.451 Å, Ca(2)-O:2.448 Å).

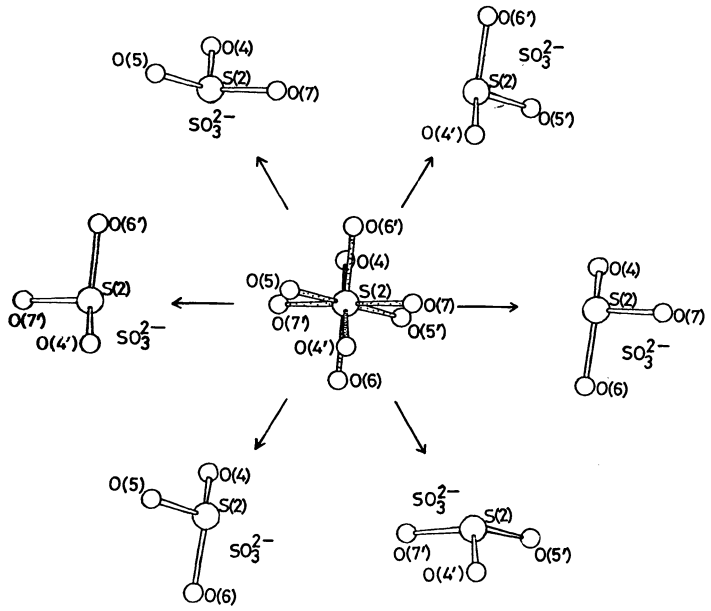

Fig. 2. Disordered-structure of SO_3^{2-}

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