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The Crystal Structure of Calcium Sulfite Tetrahydrate. Interatomic Distances and Angles

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Synopsis. Detailed geometries of the sulfite ions and of the oxygen-coordinations around the calcium ions in calcium sulfite tetrahydrate were determined based on the results of the X-ray analysis. It was revealed that the structure consists of two alternating layers, one consisting of calcium ions and water molecules, and the other consisting of sulfite ions and water molecules.

In a previous paper1) we reported the preparation, the solution and refinement of the crystal structure and the mode of disorder of a sulfite ion of calcium sulfite tetrahydrate. The interatomic distances and angles of the hydrates and anhydride of calcium sulfate were reported in detail.2–7) But no study has been reported on geometries of the sulfite ions and of the oxygen neighbors of the calcium ions in calcium sulfites. This note reports the interatomic distances and angles and the characteristic layer structure of calcium sulfite tetrahydrate.[†††]

The atomic coordinates used for the present calculations are the same as in the previous paper.1)

Results and Discussion

A projection of a part of the structure along the c axis and numbering of the atoms are shown in Fig. 1. The S(2)O$_3^{2-}$ ion is in a disordered state.1) It can be presumed that the low thermostability of the tetrahydrate is caused by the S(2)O$_3^{2-}$ ion in the disordered state.

The interatomic distances and angles are given in Tables 1 and 2. The S–O and O–O interatomic distances and O–S–O bond angles in the S(1)O$_3^{2-}$ ion are 1.52(2)—1.53(3) Å, 2.37(1)—2.39(1) Å, and 102.2(3)—102.9(4)°, respectively. The corresponding distances and angles in the S(2)O$_3^{2-}$ ion are 1.43(3)—1.44(5) Å, 2.19(4)—2.45(5) Å, and 98.9(14)—117.2(10)°, respectively. These values show that the degree of symmetry of the S(2)O$_3^{2-}$ ion is lower than that of the S(1)O$_3^{2-}$ ion. The average S(2)-O bond distance of 1.44 Å is approximately the same as the S–O bond distances in SO$_4^{2-}$ ions (calcium sulfate dihydrate 1.459 Å,2–4) calcium sulfate anhydride 1.44 Å5–7)), but is considerably short-

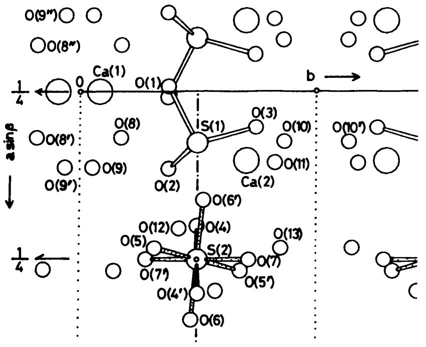

Fig. 1. Projection of the structure along the c axis and numbering of the atoms.

Table 1. Interatomic distances (l/Å) and their estimated standard deviations

Ca(1)-O(1)	2.53(1)	S(1)-O(3)	1.53(1)
Ca(1)-O(2)	2.53(7)	O(1)-O(2)	2.39(1)
Ca(1)-O(8')	2.38(5)	O(1)-O(3)	2.38(1)
Ca(1)-O(9')	2.45(1)	O(2)-O(3)	2.37(1)
Ca(1)-O(8")	2.38(5)	S(2)-O(4)	1.44(5)
Ca(1)-O(9")	2.45(1)	S(2)-O(5)	1.43(3)
Ca(2)-O(2)	2.52(1)	S(2)-O(6)	1.44(4)
Ca(2)-O(3)	2.52(3)	S(2)-O(7)	1.44(2)
Ca(2)-O(10')	2.45(1)	O(4)-O(5)	2.44(4)
Ca(2)-O(11)	2.38(1)	O(4)-O(6)	2.43(11)
Ca(2)-O(12)	2.45(1)	O(4)-O(7)	2.45(5)
Ca(2)-O(13)	2.38(9)	O(5)-O(6)	2.22(4)
Sulfite ion		O(5)-O(7)	2.25(3)
S(1)-O(1)	1.53(3)	O(6)-O(7)	2.19(4)
S(1)-O(2)	1.52(2)		

Table 2. Bond angles (ϕ/°) and their estimated standard deviations

O(1)-Ca(1)-O(2)	56.4(2)	O(13)-Ca(2)-O(3)	85.1(3)
O(1)-Ca(1)-O(9")	74.4(2)	O(13)-Ca(2)-O(12)	77.1(3)
O(9")-Ca(1)-O(8")	78.8(3)	O(13)-Ca(2)-O(11)	103.2(3)
O(8")-Ca(1)-O(9')	77.1(3)	O(13)-Ca(2)-O(10')	79.2(2)
O(9')-Ca(1)-O(2)	78.8(2)	Ca(1)-O(2)-Ca(2)	104.6(2)
O(8')-Ca(1)-O(1)	87.0(3)	Sulfite ion	
O(8')-Ca(1)-O(2)	85.1(2)	O(1)-S(1)-O(2)	102.9(4)
O(8')-Ca(1)-O(9")	77.1(3)	O(1)-S(1)-O(3)	102.2(3)
O(8')-Ca(1)-O(8")	102.5(3)	O(2)-S(1)-O(3)	102.3(4)
O(8')-Ca(1)-O(9')	78.8(3)	O(4)-S(2)-O(5)	117.2(10)
O(2)-Ca(2)-O(3)	56.3(2)	O(4)-S(2)-O(6)	115.7(13)
O(12)-Ca(2)-O(2)	74.7(3)	O(4)-S(2)-O(7)	117.1(10)
O(11)-Ca(2)-O(12)	78.8(3)	O(5)-S(2)-O(6)	102.0(14)
O(10')-Ca(2)-O(11)	77.1(3)	O(5)-S(2)-O(7)	103.2(15)
O(3)-Ca(2)-O(10')	78.9(3)	O(6)-S(2)-O(7)	98.9(14)
O(13)-Ca(2)-O(2)	86.5(2)		

[†††] The anisotropic temperature factors and the complete F_o—F_c data are deposited as Document No. 8405 at the Office of the Editor of Bull. Chem. Soc. Jpn.

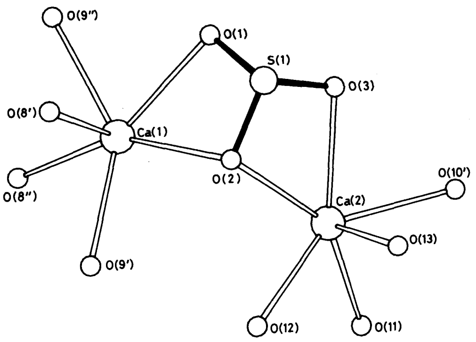

Fig. 2. Environment of the calcium ions.

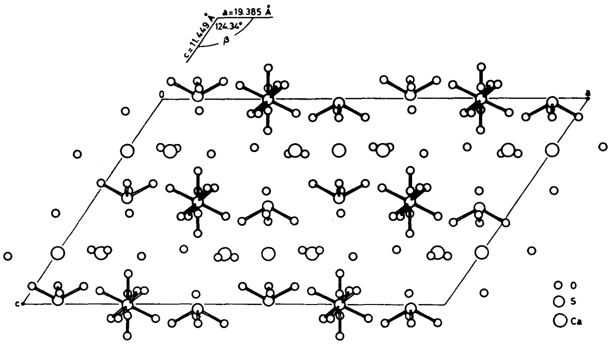

Fig. 3. Projection of the structure along the b axis.

er than 1.53 Å in the $S(1)O_3^{2-}$ ion. One of the reasons for the difference of the S–O bond distances between $S(1)O_3^{2-}$ and $S(2)O_3^{2-}$ may be that only the O atoms of the $S(1)O_3^{2-}$ ion coordinate to the Ca^{2+} ions (*cf.* Fig. 2). Another reason may be that, in many cases, the interatomic distances and angles calculated from the coordinates of the atoms which are in a disordered state give rise to apparent deviations from the usual values.

The coordinations of the O atoms around the Ca^{2+} ions are shown in Fig. 2. Both Ca(1) and Ca(2) are coordinated by six O atoms in distorted octahedral arrangements: two O atoms originate from the $S(1)O_3^{2-}$ ion, and the other four from water molecules. The Ca(1)–O(1) distance is almost the same as the Ca(1)–O(2) distance. The Ca(1)–O(9′) and Ca(1)–O(9″), and the Ca(1)–O(8′) and Ca(1)–O(8″) distances are the same, respectively. The Ca(2)–O distances are similar to the Ca(1)–O distances; the average values are both 2.45 Å. These Ca–O distances are close to those (2.378—2.544 Å) in calcium sulfate dihydrate.[2–4] The O–Ca(2)–O bond angles are also similar to the corresponding O–Ca(1)–O angles. Thus, the geometries of the Ca(1)–O and Ca(2)–O coordinations resemble each other very closely.

The crystal structure viewed along the b axis is shown in Fig. 3. It is observed that two layers, one consisting of the Ca^{2+} ions and water molecules, and the other consisting of the SO_3^{2-} ions and water molecules, arrange alternately parallel to the (001) plane.

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