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STUDIES ON ALKALINE EARTH SULFITES. VII. (1) HYDROGEN BONDING AND THE LOCATION OF HYDROGEN ATOMS IN THE CRYSTAL STRUCTURE OF $CaSO_3 \cdot 4H_2O$ AND $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$

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The location of the hydrogen atoms in the crystal structure of $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ was calculated using structural considerations. The results were confirmed by the agreement in the intensities of the X-ray powder diffraction lines between the calculated and the measured patterns. The orientation of the water molecules is such as to allow maximal hydrogen bonding of all oxygens belonging to SO_3^{2-} or SO_4^{2-} groups. Also, the coordination of the ca-atoms is shown to be eight and not six as previously reported.

In the crystal structure reported for calcium sulfite tetrahydrate(2,3) and the double-salt $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$,(4) the location of the hydrogen atoms was omitted. This is due to the difficulty in ascertaining the location of hydrogen atoms by X-ray diffraction, especially in molecules showing a large degree of disorder. We now report an attempt to locate the sites of the hydrogen atoms by calculations based on structural considerations.

As previously shown,(2,4) the crystal structure of the studied salts contains two types of sulfur atoms, S(1) and S(2). The latter sulfur belongs to a sulfite group in $CaSO_3 \cdot 4H_2O$ and to a sulfate group in $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$. While the oxygens surrounding S(1) are within bond-forming distance of the calcium atoms, the oxygens around S(2) cannot have any bonds to calcium. In order to give the structure some stability, the latter oxygens must be assumed to participate in hydrogen bonding with the water molecules. Maximum stability will be ensured if each oxygen atom around S(2) participates in three such bonds, involving all outer electron pairs except the one forming the bond with S(2).

It should be noted that, contrary to Matsuno et al.,(2,3) the coordination of the calcium atoms is eight and not six, since no less than four $S(1)O_3^{2-}$ oxygens and four H_2O oxygens are within 2.38-2.52 Å of each Ca-atom. The oxygen configuration around the Ca-atoms is a distorted tetragonal Archimedean antiprism,(5) with all edges but two having a length of 3.01-3.37 Å. The eight-coordinated structure of the Ca-atoms and selected inter atomic distances are shown in a schematic diagram, Fig. 1. It follows that each $S(1)O_3^{2-}$ oxygen is bound to two Ca-atoms in addition to the S-O bond, which leaves one electron pair free for hydrogen bonding.

On the other hand, the stability of such highly hydrated salts will be increased by a maximum participation of the hydrogens in hydrogen bonds, and they should, therefore, be located where they can participate in such bonding.

Calculation of interatomic distances in the crystal shows indeed that all sites available to oxygens around S(2) are within 2.64-2.87 Å of three different water oxygens, which is the optimum distance for hydrogen bonding.[6] Also, each $S(1)O_3^{2-}$ oxygen is at 2.71-2.75 Å from one water oxygen. We may, therefore, conclude that maximal hydrogen bonding does occur.

Taking the O-H distance in a water molecule as 0.98-1.06 Å for H-atoms participating in a H-bond (and otherwise as 0.94 Å), and the hydrogen bond distance H•••O as 1.66-1.81 Å, we arrive at the location of the hydrogen atoms as given in Table 1. The accuracy of the coordinates in Table 1 is estimated at ±0.002, corresponding to a maximum deviation of 0.05 Å for any H-atom in any direction. Interatomic distances and bond angles involving the H-atoms are given in Tables 2 and 3 respectively.

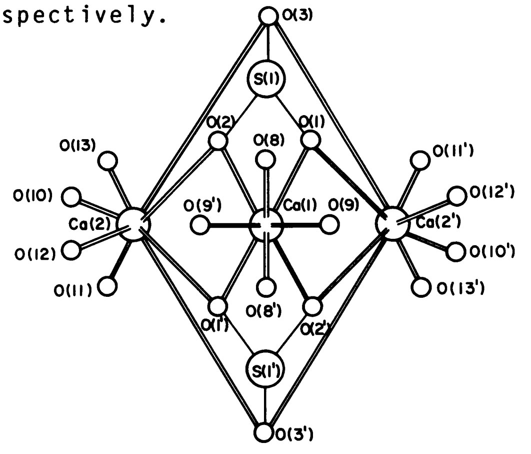

FIG. 1. EIGHT-COORDINATED STRUCTURE OF Ca-ATOMS IN $CaSO_3.4H_2O$.

The three Ca-atoms should be seen as the vertices of a nearly equilateral triangle perpendicular to the axis S(1)-S(1') which is in the plane of the figure. O(1), O(2), and O(3), and similarly O(1'), O(2'), and O(3') also form equilateral triangles perpendicular to S(1)-S(1'). In other words, the planes O(1)-O(2)-O(3), Ca(1)-Ca(2)-Ca(2'), and O(1')-O(2')-O(3') are parallel. Interatomic distances (Å), and their estimated standard deviations,[a] involving O-atoms around Ca(1) and Ca(2) are given below:

Ca(1)-O distances	
Ca(1)-O(1) Ca(1)-O(1')	2.525(7)
Ca(1)-O(2) Ca(1)-O(2')	2.525(6)
Ca(1)-O(8) Ca(1)-O(8')	2.379(6)
Ca(1)-O(9) Ca(1)-O(9')	2.450(8)

Ca(2)-O distances	
Ca(2)-O(2)	2.520(5)
Ca(2)-O(3')	2.516(4)
Ca(2)-O(3)	2.515(8)
Ca(2)-O(1')	2.521(5)
Ca(2)-O(13)	2.377(10)
Ca(2)-O(11)	2.377(6)
Ca(2)-O(12)	2.451(5)
Ca(2)-O(10)	2.449(5)

O-O distances around Ca(1)	
O(1)-O(2) O(1')-O(2')	2.385(4)
O(1)-O(2') O(1')-O(2)	3.051(12)
O(8)-O(9) O(8')-O(9')	3.009(9)
O(8)-O(9') O(8')-O(9)	3.067(15)
O(1)-O(8) O(1')-O(8')	3.375(8)
O(1)-O(9) O(1')-O(9')	3.007(9)
O(2)-O(8) O(2')-O(8')	3.321(11)
O(2)-O(9') O(2')-O(9)	3.161(7)

O-O distances around Ca(2)	
O(2)-O(3)	2.374(7)
O(3')-O(1')	2.379(10)
O(2)-O(1')	3.051(12)
O(3')-O(3)	3.027(12)
O(13)-O(12)	3.010(9)
O(11)-O(10)	3.007(16)
O(13)-O(10)	3.077(9)
O(11)-O(12)	3.062(10)
O(2)-O(13)	3.359(8)
O(3')-O(11)	3.364(14)
O(2)-O(12)	3.018(13)
O(3')-O(10)	3.005(9)
O(3)-O(13)	3.316(4)
O(1')-O(11)	3.300(14)
O(3)-O(10)	3.158(13)
O(1')-O(12)	3.152(7)

[a] Calculated from atomic coordinates and their standard deviations reported by Matsuno et al.[2]

Table 1. Calculated atomic coordinates of hydrogen atoms, their atomic occupancies and bondings, in $CaSO_3\cdot4H_2O$ and $Ca_3(SO_3)_2SO_4\cdot12H_2O$

Atom	Atomic coordinates[a]			Occup.	Bound to O_{water}[b]	Hydrogen-bonded to[b]
	X	Y	Z			
H(1)	0.130	0.155	-0.008	1/2	O(8)	O(5)
H(2)	0.103	0.153	-0.059	1/2	O(8)	O(6)
H(3)	0.047	0.126	-0.001	1	O(8)	O(1)
H(4)	0.146	0.110	-0.223	1/2	O(9)	O(4)
H(5)	0.164	0.071	-0.192	1/2	O(9)	O(7)
H(6)	0.141	-0.015	-0.300	1	O(9)	-
H(7)	0.121	0.364	-0.224	1/2	O(10)	O(4)
H(8)	0.107	0.369	-0.193	1/2	O(10)	O(6)
H(9)	0.022	0.397	-0.300	1	O(10)	-
H(10)	0.126	0.357	0.009	1/2	O(11)	O(6)
H(11)	0.159	0.392	0.059	1/2	O(11)	O(7)
H(12)	0.086	0.492	0.001	1	O(11)	O(3)
H(13)	0.240	0.226	0.223	1/2	O(12)	O(4)
H(14)	0.215	0.192	0.192	1/2	O(12)	O(5)
H(15)	0.213	0.132	0.300	1	O(12)	-
H(16)	0.255	0.012	0.059	1/2	O(13)	O(5)
H(17)	0.261	0.005	0.008	1/2	O(13)	O(7)
H(18)	0.211	-0.117	0.001	1	O(13)	O(2)

[a] The accuracy is estimated at ±0.002.

[b] For atomic coordinates of water and SO_3^{2-} oxygens, see Matsuno et al.[2]

Table 2. Interatomic distances[a] (Å) involving H-atoms, and their estimated standard deviations, in $CaSO_3\cdot4H_2O$ and $Ca_3(SO_3)_2SO_4\cdot12H_2O$

O(8)-H(1)	1.03(2)	O(1)--H(3)	1.73(1)	H(1)...H(3)	1.67(4)
O(8)-H(2)	1.00(2)	O(2)--H(18)	1.73(1)	H(2)...H(3)	1.60(5)
O(8)-H(3)	1.01(1)	O(3)--H(12)	1.74(1)	H(4)...H(6)	1.63(4)
O(9)-H(4)	1.05(3)	O(4)--H(4)	1.79(4)	H(5)...H(6)	1.42(5)
O(9)-H(5)	0.98(2)	O(4)--H(7)	1.81(4)	H(7)...H(9)	1.65(3)
O(9)-H(6)	0.94(2)	O(4)--H(13)	1.78(3)	H(8)...H(9)	1.43(4)
O(10)-H(7)	1.06(3)	O(5)--H(1)	1.74(3)	H(10)...H(12)	1.68(3)
O(10)-H(8)	1.00(2)	O(5)--H(14)	1.68(4)	H(11)...H(12)	1.62(4)
O(10)-H(9)	0.94(2)	O(5)--H(16)	1.72(3)	H(13)...H(15)	1.62(4)
O(11)-H(10)	1.02(2)	O(6)--H(2)	1.70(2)	H(14)...H(15)	1.40(5)
O(11)-H(11)	1.03(2)	O(6)--H(8)	1.70(3)	H(16)...H(18)	1.62(3)
O(11)-H(12)	1.02(1)	O(6)--H(10)	1.74(3)	H(17)...H(18)	1.65(3)
O(12)-H(13)	1.05(3)	O(7)--H(5)	1.66(4)		
O(12)-H(14)	0.99(2)	O(7)--H(11)	1.75(3)		
O(12)-H(15)	0.94(2)	O(7)--H(17)	1.71(3)		
O(13)-H(16)	1.01(2)				
O(13)-H(17)	1.01(2)				
O(13)-H(18)	1.02(1)				

[a] -, covalent bond; --, coordination or hydrogen bond; ..., no bond.

Table 3. Bond angles[a)] (°) involving H-atoms, and their estimated standard deviations, in $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$

H(1)-O(8)-H(3)	110(3)	Ca(1)--O(8)-H(1)	122(2)	Ca(2)--O(12)-H(14)	128(2)	S(1)-O(1)--H(3)	125(1)
H(2)-O(8)-H(3)	106(3)	Ca(1)--O(8)-H(2)	116(2)	Ca(2)--O(12)-H(15)	127(2)	S(1)-O(2)--H(18)	125(1)
H(4)-O(9)-H(6)	110(4)	Ca(1)--O(8)-H(3)	128(1)	Ca(2)--O(13)-H(16)	115(2)	S(1)-O(3)--H(12)	124(1)
H(5)-O(9)-H(6)	96(4)	Ca(1)--O(9)-H(4)	126(2)	Ca(2)--O(13)-H(17)	123(2)	S(2)-O(4)--H(4)	113(3)
H(7)-O(10)-H(9)	111(3)	Ca(1)--O(9)-H(5)	127(2)	Ca(2)--O(13)-H(18)	128(1)	S(2)-O(4)--H(7)	112(3)
H(8)-O(10)-H(9)	95(3)	Ca(1)--O(9)-H(6)	127(1)			S(2)-O(4)--H(13)	113(2)
H(10)-O(11)-H(12)	111(3)	Ca(2)--O(10)-H(7)	125(2)			S(2)-O(5)--H(1)	119(3)
H(11)-O(11)-H(12)	104(3)	Ca(2)--O(10)-H(8)	128(2)	Ca(1)--O(1)--H(3)	114(1)	S(2)-O(5)--H(14)	123(4)
H(13)-O(12)-H(15)	109(4)	Ca(2)--O(10)-H(9)	127(2)	Ca(1)--O(2)--H(18)	110(1)	S(2)-O(5)--H(16)	121(3)
H(14)-O(12)-H(15)	94(4)	Ca(2)--O(11)-H(10)	125(2)	Ca(2)--O(2)--H(18)	113(1)	S(2)-O(6)--H(2)	122(2)
H(16)-O(13)-H(18)	106(3)	Ca(2)--O(11)-H(11)	116(2)	Ca(2)--O(3')--H(12')	113(1)	S(2)-O(6)--H(8)	121(3)
H(17)-O(13)-H(18)	109(3)	Ca(2)--O(11)-H(12)	127(1)	Ca(2)--O(3)--H(12)	110(1)	S(2)-O(6)--H(10)	119(3)
		Ca(2)--O(12)-H(13)	125(2)	Ca(2)--O(1')--H(3')	110(1)	S(2)-O(7)--H(5)	125(4)
						S(2)-O(7)--H(11)	118(3)
						S(2)-O(7)--H(17)	121(3)

[a)] -, covalent bond; --, coordination or hydrogen bond.

As stated previously, there are six (or possibly eight) different orientations available to $S(2)O_3^{2-}$,[2)] and two orientations to $S(2)O_4^{2-}$.[4)] We should assume that the orientation of the various water molecules adapts itself to that of the $S(2)O_3^{2-}$ or $S(2)O_4^{2-}$ groups so as to ensure maximum hydrogen bonding. Therefore, hydrogen atoms involved in H-bonds with oxygens of these groups will occupy alternative sites depending on the occupied oxygen sites. Such alternation exists between H(1)-H(2), H(4)-H(5), H(7)-H(8), H(10)-H(11), H(13)-H(14), and H(16)-H(17). In $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$, all hydrogen atoms in either of these sites will participate in an H-bond, while in $CaSO_3 \cdot 4H_2O$ only $^3/_4$ of these hydrogen atoms will find an oxygen atom available for H-bonding. Adding the hydrogen bonds involving $S(1)O_3^{2-}$ oxygens, it can be seen that $^5/_8$ of all hydrogens in $CaSO_3 \cdot 4H_2O$ and $^3/_4$ of all hydrogens in $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ participate in H-bonds. In other words, H-bonding involves 60 (out of 96) H-atoms in a unit-cell of $CaSO_3 \cdot 4H_2O$, containing 12 formula units, and 72 H-atoms in a unit-cell of $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$, containing 4 formula units.

The hydrogen atoms H(6), H(9), and H(15) are not within H-bonding distance of any oxygen atom. Their locations were, therefore, determined according to considerations involving the H-O-H angle in a water molecule (94 °-111 °),[6)] taking into account both alternative sites of the other hydrogen atom, and the average Ca--O-H angle (121 ° ± 7 °) as calculated for all other H-atoms. It thus appears that all hydrogen atoms are arranged in a small number of planes, approximately parallel to the x-y plane. This arrangement is similar to that found for Ca-atoms, $S(1)O_3^{2-}$-oxygens, $S(2)O_3^{2-}$-oxygens and H_2O-oxygens, using the atomic coordinates reported by Matsuno et al.[2)]

The complete crystal structures of $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$, including the hydrogen atoms, were introduced into the LAZY-PULVERIX computer program[7)] for calculating the X-ray powder diffraction patterns. Table 4 shows the calculated pattern for $CaSO_3 \cdot 4H_2O$ compared to one calculated by the same program without including the H-atoms,[4)] and to the actual measured diffractogram.[8)] It should be taken into account that all observed intensities are given in relation to the combined line $\{200 + 11\bar{1}\}$ = 100%, while the calculated intensities are given in relation to $\{11\bar{1}\}$ = 100%, the intensity of {200} being 50%. We should therefore expect the calculated intensities to be larger than the observed ones by a factor of $^3/_2$.

It can be seen that inclusion of the hydrogen atoms at their calculated sites yields a large improvement in the agreement between the calculated and the measured

Table 4. Observed[a] and Calculated[b] X-ray powder diffraction patterns of $CaSO_3\cdot4H_2O$

	Obsd		Calcd				Obsd		Calcd				Obsd		Calcd		
h k ℓ	d(Å)	I[c]	d(Å)	I[d]		h k ℓ	d(Å)	I[c]	d(Å)	I[d]		h k ℓ	d(Å)	I[c]	d(Å)	I[d]	
2 0 0	8.201	100	8.003	50	50	3 3 $\bar{3}$			2.667	42	54	10 0 $\bar{4}$			1.920	4	5
1 1 $\bar{1}$			8.001	100	100	6 0 $\bar{4}$			2.667	14	19	4 2 3	1.873	12	1.875	3	4
1 1 1	5.742	125	5.723	79	95	5 3 0	2.430	18	2.429	6	8	1 3 4			1.874	3	3
2 0 $\bar{2}$			5.723	40	48	2 4 1			2.429	6	8	5 1 $\bar{6}$			1.874	3	3
0 2 0	5.602	52	5.596	32	32	7 1 $\bar{4}$			2.429	6	8	10 0 $\bar{2}$			1.870	4	4
3 1 $\bar{1}$			5.596	64	63	6 2 0	2.409	5	2.408	2	2	5 5 $\bar{3}$			1.870	6	8
3 1 0	4.819	25	4.816	9	8	0 4 2			2.408	2	2	5 3 2			1.861	3	4
0 2 1			4.816	10	8	6 2 $\bar{4}$			2.408	2	2	2 4 3			1.861	3	4
3 1 $\bar{2}$			4.815	9	8	0 0 4	2.370	21	2.363	17	25	7 1 $\bar{6}$			1.860	3	4
0 0 2			4.727	1	2	7 1 0	2.242	18	2.240	5	6	9 3 $\bar{2}$	1.830	12	1.830	6	7
2 2 0	4.587	16	4.586	13	16	2 4 $\bar{3}$			2.240	5	6	0 6 1			1.830	6	7
4 0 $\bar{2}$			4.585	7	9	5 3 $\bar{4}$			2.240	5	6	9 3 $\bar{4}$			1.830	6	7
4 0 0	4.008	4	4.002	1	1	7 3 $\bar{2}$	2.217	16	2.217	6	8	10 2 $\bar{3}$			1.828	2	3
2 2 $\bar{2}$			4.001	2	3	1 5 0			2.217	6	8	2 6 $\bar{1}$			1.828	2	3
4 2 $\bar{1}$			3.633	8	9	8 2 $\bar{3}$			2.217	7	8	8 4 $\bar{3}$			1.828	2	3
1 3 0			3.633	8	9	8 2 $\bar{2}$			2.197	3	3	3 1 4	1.798	11	1.791	2	3
5 1 $\bar{2}$			3.633	8	9	1 5 $\bar{1}$			2.197	3	3	0 2 5			1.791	2	3
3 1 1	3.619	112	3.612	31	34	7 3 $\bar{3}$			2.197	3	3	3 1 $\bar{6}$			1.791	2	3
0 2 2			3.611	31	35	7 3 $\bar{1}$			2.122	3	3	1 1 5	1.750	4	1.744	2	3
3 1 $\bar{3}$			3.610	31	35	1 5 1			2.122	3	3	2 0 $\bar{6}$			1.744	1	2
3 3 $\bar{1}$	3.236	38	3.231	34	47	8 2 $\bar{4}$			2.122	3	3	9 3 $\bar{1}$	1.738	16	1.735	6	6
6 0 $\bar{2}$			3.231	17	24	3 5 $\bar{1}$	2.113	25	2.115	4	6	0 6 2			1.735	6	6
5 1 0	3.085	30	3.078	10	14	6 4 $\bar{2}$			2.115	4	5	9 3 $\bar{5}$			1.735	5	6
1 3 $\bar{2}$			3.077	11	15	9 1 $\bar{3}$			2.115	4	6	5 5 1	1.700	5	1.701	2	3
4 2 $\bar{3}$			3.077	11	15	5 1 2			2.109	5	6	10 0 $\bar{6}$			1.701	1	2
2 2 2	2.872	62	2.862	24	32	1 3 $\bar{4}$			2.108	5	6	6 6 $\bar{2}$			1.615	7	8
4 0 $\bar{4}$			2.861	11	15	4 2 $\bar{5}$			2.108	5	5	12 0 $\bar{4}$			1.615	4	4
3 1 2	2.757	5	2.746	1	1	6 2 1	2.093	36	2.093	14	17	10 0 0			1.601	2	2
0 2 3			2.746	1	1	0 4 3			2.092	14	17	5 5 $\bar{5}$			1.600	4	4
3 1 $\bar{4}$			2.745	1	1	6 2 $\bar{5}$			2.092	14	17	9 1 1	1.578	16	1.576	5	6
4 2 1	2.724	54	2.718	15	22	8 0 0	2.001	4	2.001	1	1	6 4 2			1.576	3	3
1 3 2			2.717	15	23	4 4 $\bar{4}$			2.000	2	3	3 5 3			1.576	3	3
5 1 $\bar{4}$			2.717	15	22	2 0 4	1.988	9	1.983	2	3	3 5 $\bar{5}$			1.576	5	6
6 0 0	2.673	102	2.668	21	27	1 1 $\bar{5}$			1.983	4	5	6 4 $\bar{6}$			1.576	5	6
3 3 1			2.668	29	38	5 5 $\bar{1}$	1.921	14	1.921	10	11	9 1 $\bar{7}$			1.576	3	3

[a] Reported by Shiino et al.[8]

[b] Using the LAZY-PULVERIX computer program,[7] calculated from atomic coordinates, atomic occupancies, temperature factors and unit-cell dimensions as given by Matsuno et al.,[2] and atomic coordinates and occupancies for the hydrogen atoms as given in Table 1.

[c] In order to allow a comparison with the calculated patterns, the intensity of the line {200 + 11$\bar{1}$} was fixed at 100% and the other lines adjusted accordingly.

[d] The left column - calculated excluding the hydrogen atoms, the right column - including the hydrogen atoms.

intensities of the various diffraction lines. We may, therefore, be confident that the calculated location of the hydrogen atoms is approximately correct.

We may conclude that in highly hydrated crystals, where the hydrogen atoms cannot be located by X-ray diffraction because of a disordered structure, it could still be possible to calculate their location using structural considerations, assuming maximum H-bonding. This work completes the determination of the crystalline structure of $CaSO_3\cdot4H_2O$ and $Ca_3(SO_3)_2SO_4\cdot12H_2O$ and shows that H-bonding is the only factor stabilizing the $S(2)O_3^{2-}$ or $S(2)O_4^{2-}$ groups in this structure.

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