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STUDIES ON ALKALINE EARTH SULFITES - V. 1) STRUCTURE AND STABILITY OF THE NEW COMPOUND $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$ AND ITS SOLID SOLUTION IN CALCIUM SULFITE TETRAHYDRATE

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The hitherto unknown double-salt $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$ and its solid solution in $CaSO_3{\cdot}4H_2O$ are reported. The new salts were prepared from aqueous solutions at 3-5 °C and studied by chemical analysis, thermal analysis and X-ray powder diffraction. Chemical compositions, dehydration temperatures, calculated and measured X-ray diffraction patterns and lattice parameters are presented and discussed. The crystallographic structure of the double-salt is very similar to that of $CaSO_3{\cdot}4H_2O$, but the thermal stability of the former is higher.

A number of early references report the formation of calcium sulfite dihydrate.2,3) However, later investigators found no evidence of its existence but isolated a hemihydrate.4,5) In an attempt to repeat the work of the early authors, solutions of $NaHSO_3$ and $CaCl_2$ were reacted at low temperatures. In one of our trials an unfresh $NaHSO_3$ solution was used and, as a result, a highly hydrated mixed sulfite-sulfate calcium salt with an unknown X-ray powder diffraction pattern was obtained.6) Chemical and thermal analyses of this salt showed the possible existence of a new type of calcium sulfite-calcium sulfate solid solution, $(CaSO_3{\cdot}4H_2O)_m$ - $(CaSO_4{\cdot}4H_2O)_n$ where $m > 2n$. This paper presents chemical, thermogravimetric and crystallographic studies of the new compound $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$ and its solid solution in $CaSO_3{\cdot}4H_2O$.

Four samples were prepared (A-D) at 3-5 °C. 100 ml of 1 M aqueous solutions, consisting of Na_2SO_3 and Na_2SO_4 in various ratios, were stirred into 100 ml of 1 M aqueous solutions of $CaCl_2$. It should be noted that attempts to prepare samples with a desired SO_4^{2-}/SO_3^{2-} ratio were unsuccessful when solutions of $CaCl_2$ and Na_2SO_3/Na_2SO_4 were dropped simultaneously into the reaction vessel and also when the $CaCl_2$ solution was dropped into the Na_2SO_3/Na_2SO_4 solution.7) All reagents used were of analytical purity. The samples were washed several times with O_2-free distilled water at 3 °C, dried between filter paper at room temperature and kept at 0 °C for characterization.

Table 1 gives the chemical composition of samples A-D. It is evident that sample C has a chemical composition corresponding to the theoretical composition of $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$. In comparison with sample C, samples A and B have a lower sulfate content and sample D has a higher sulfate content.

Recently two teams, investigating the effect of minute amounts of additives on the morphology of $CaSO_3{\cdot}0.5H_2O$ particles, reported8,9) simultaneously the existence of $CaSO_3{\cdot}4H_2O$. Very recently Shiino et al.10) reported that $CaSO_3{\cdot}4H_2O$ crystallizes in the rhombohedral system, but Matsuno et al.11) determined its crystalline structure, from reliable structure analysis, as monoclinic. In order to analyse Shiino's data, we submitted his reported X-ray powder diffraction data to Visser's computer program12) (a program used to determine the unit cell from powder data). The program shows only the monoclinic structure to be compatible with a high degree of reliability, while the rhombohedral unit cell, proposed by Shiino,10) is rejected. These results were further confirmed by reverse calculation using the LAZY-PULVERIX computer program,13) a program for calculating X-ray and neutron diffraction powder patterns. Starting with the monoclinic crystalline structure given by Matsuno et al.,[11)] a calculated diffractogram, in agreement with that measured by Shiino,[10)] was obtained.

Table 2 gives the atomic occupancies and the equivalent isotropic temperature factors, determined by Matsuno,[11)] used for calculating the X-ray diffraction patterns of $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$. In calculating the latter pattern, the occupancy of all the oxygens of S(2) was adjusted to 0.5 on replacing SO_3^{2-} with SO_4^{2-} , and their temperature factors were assumed to be 2.0 owing to their reduced disordered orientation state. The calculated and the observed X-ray diffraction patterns are given in Table 3. It is clear that the X-ray diffraction pattern of the $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ is very similar to that of $CaSO_3 \cdot 4H_2O$.[14)] This is not surprising since, in the structure of $CaSO_3 \cdot 4H_2O$, 1/3 of the sulfur atoms, S(2), have four possible sites for oxygen atoms, O(4) - O(7), in positions which permit σ-bonds with the sulfur atom.[11)] The configuration of these sites resembles that of the oxygen atoms in the SO_4^{2-} ion. This was explained[11)] by assuming that the sulfite ions, $S(2)O_3^{2-}$, are in a state of disordered orientation, and their oxygen atoms occupy sites of partial occupancy (Table 2); so that, we presume, they could easily be replaced by sulfate ions, merely increasing the occupancy of the oxygen sites (Table 2).

We, therefore, conclude that our products are:

(1) A double-salt, $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ (sample C).

(2) Solid solutions of this double-salt with $CaSO_3 \cdot 4H_2O$ (samples A and B).

(3) A solid solution obtained by a partial substitution of SO_3^{2-} ions with SO_4^{2-} ions in $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ (sample D).

Table 1. Results of chemical analyses[a)] of $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ and its solid solutions

Sample	Composition (wt%)					Mole ratio
	CaO	SO_2	SO_3	H_2O	Total	(SO_3/CaO)
A	29.1	24.6	10.8	35.4	99.9	0.260
B	28.4	22.9	11.9	36.5	99.7	0.294
C	28.3	21.6	13.4	36.5	99.8	0.332
D	28.1	20.0	15.2	36.3	99.6	0.378
Theoretical values for $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ are:	28.39	21.62	13.51	36.48	100.00	0.3333

[a)] Sulfite was determined by iodometry, calcium by complexometry with EDTA using methylthymol blue as indicator, and water by thermogravimetry. The amount of sulfate was calculated as the difference between calcium and sulfite values.

Table 2. Atomic occupancies and equivalent isotropic temperature factors used for calculating the X-ray diffraction patterns of $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$

Atom[a)]	No.[b)]	Occup.[c)]		$B_{eq}(Å^2)$[c)]	
Ca(1)	4	1	1	0.8	0.8
Ca(2)	8	1	1	0.7	0.7
S (1)	8	1	1	0.1	0.1
S (2)	4	1	1	3.0	1.5
O (1)	8	1	1	0.8	0.8
O (2)	8	1	1	0.9	0.9
O (3)	8	1	1	0.8	0.8
O (4)	8	1/2	1/2	2.7	2.0
O (5)	8	1/3	1/2	6.6	2.0
O (6)	8	1/3	1/2	4.5	2.0
O (7)	8	1/3	1/2	5.2	2.0
O (8)	8	1	1	2.8	2.8
O (9)	8	1	1	1.9	1.9
O(10)	8	1	1	1.9	1.9
O(11)	8	1	1	3.9	3.9
O(12)	8	1	1	1.9	1.9
O(13)	8	1	1	1.2	1.2

[a)] σ-bondings exist between S(1) and O(1)-O(3), and between S(2) and O(4)-O(7); O(4)-O(13) belong to H_2O molecules.

[b)] Number of atoms in unit cell for occupancy 1.

[c)] The left column - $CaSO_3 \cdot 4H_2O$, the right column - $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$.

The unit cell dimensions of samples A-D were calculated from their respective diffraction patterns and are given in Table 4. The change in lattice parameters of $CaSO_3 \cdot 4H_2O$, obtained on substituting SO_3^{2-} with SO_4^{2-} , is shown in Fig. 1. It can be seen that a gradual expansion of the three dimensions of the $CaSO_3 \cdot 4H_2O$ lattice occurs when SO_3^{2-} ions are substituted with SO_4^{2-} ions, up to a substitution of 1/3 of the sulfite ions. Further substitution results in a slight contraction along dimensions a and b, and a sharp expansion along dimension c. This behaviour can be expected since, in such further substitution, sulfite ions of a different type, $S(1)O_3^{2-}$, are replaced.

The four oxygen sites around S(2), contrary to those around S(1), are not within bond-forming distance of the Ca-atoms, and are assumed to participate in hydrogen bonding with the water molecules. This bonding is substantially increased in $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$ as compared to $CaSO_3 \cdot 4H_2O$; but stability is further increased by the threefold reduction in orientational disorder (two possible orientations instead of six[11)]) obtained in replacing $S(2)O_3^{2-}$ with $S(2)O_4^{2-}$. This increased stability manifests itself in the following ways:

(1) The double-salt can be prepared without the addition of additives like sodium citrate.

Table 3. Calculated[a] and observed[b] X-ray powder diffraction patterns of $CaSO_3\cdot 4H_2O$ and $Ca_3(SO_3)_2SO_4\cdot 12H_2O$

	$CaSO_3\cdot 4H_2O$				$Ca_3(SO_3)_2SO_4\cdot 12H_2O$			
	Calcd		Obsd		Calcd		Obsd	
h k l	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
2 0 0	8.003	50	8.201	80	8.073	33	8.079	44
1 1 $\bar{1}$	8.001	100			8.076	66		
1 1 1	5.723	79	5.742	100	5.764	100	5.770	100
2 0 $\bar{2}$	5.723	40			5.767	51		
0 2 0	5.596	32	5.602	42	5.656	40	5.651	31
3 1 $\bar{1}$	5.596	64			5.656	79		
3 1 0	4.816	9	4.819	20	4.860	9	4.863	16
0 2 1	4.816	10			4.861	10		
3 1 $\bar{2}$	4.815	9			4.862	9		
0 0 2	4.727	1			4.754	3	4.748	1
2 2 0	4.586	13	4.587	13	4.632	16	4.631	11
4 0 $\bar{2}$	4.585	7			4.634	9		
4 0 0	4.002	1	4.008	3	4.036	1	4.044	2
2 2 $\bar{2}$	4.001	2			4.038	1		
4 2 $\bar{1}$	3.633	8			3.672	8	3.669	14
1 3 0	3.633	8			3.672	8		
5 1 $\bar{2}$	3.633	8			3.672	8		
3 1 1	3.612	31	3.619	90	3.638	35	3.639	67
0 2 2	3.611	31			3.639	35		
3 1 $\bar{3}$	3.610	31			3.640	35		
3 3 $\bar{1}$	3.231	34	3.236	30	3.265	35	3.263	19
6 0 $\bar{2}$	3.231	17			3.266	18		
5 1 0	3.078	10	3.085	24	3.105	11	3.107	19
1 3 $\bar{2}$	3.077	11			3.106	11		
4 2 $\bar{3}$	3.077	11			3.107	11		
2 2 2	2.862	24	2.872	50	2.882	23	2.882	23
4 0 $\bar{4}$	2.861	11			2.884	11		
3 1 2	2.746	1	2.757	4	2.764	1	2.774	3
0 2 3	2.746	1			2.765	1		
3 1 $\bar{4}$	2.745	1			2.766	1		
4 2 1	2.718	15	2.724	43	2.740	14	2.742	27
1 3 2	2.717	15			2.740	15		
5 1 $\bar{4}$	2.717	15			2.741	14		
6 0 0	2.668	21	2.673	82	2.691	23	2.693	63
3 3 1	2.668	29			2.691	28		
3 3 $\bar{3}$	2.667	42			2.692	46		
6 0 $\bar{4}$	2.667	14			2.693	14		
5 3 0	2.429	6	2.430	14	2.453	7	2.453	12
2 4 1	2.429	6			2.453	7		
7 1 $\bar{4}$	2.429	6			2.454	6		
6 2 0	2.408	2	2.409	4	2.430	2	2.432	3
0 4 2	2.408	2			2.430	2		
6 2 $\bar{4}$	2.408	2			2.431	2		
0 0 4	2.363	17	2.370	17	2.377	17	2.375	9
7 1 0	2.240	5	2.242	14	2.260	5	2.261	7
2 4 $\bar{3}$	2.240	5			2.261	5		
5 3 $\bar{4}$	2.240	5			2.261	5		
7 3 $\bar{2}$	2.217	6	2.217	13	2.240	6	2.239	5
1 5 0	2.217	6			2.240	6		
8 2 $\bar{3}$	2.217	7			2.241	7		
8 2 $\bar{2}$	2.197	3			2.220	3	2.219	3
1 5 $\bar{1}$	2.197	3			2.220	3		
7 3 $\bar{3}$	2.197	3			2.220	3		
7 3 $\bar{1}$	2.122	3			2.143	3	2.142	7
1 5 1	2.122	3			2.143	3		
8 2 $\bar{4}$	2.122	3			2.144	3		
3 5 $\bar{1}$	2.115	4	2.113	20	2.138	4	2.138	8
6 4 $\bar{2}$	2.115	4			2.138	3		
9 1 $\bar{3}$	2.115	4			2.138	4		
5 1 2	2.109	5			2.124	5	2.122	10
1 3 $\bar{4}$	2.108	5			2.124	5		
4 2 $\bar{5}$	2.108	5			2.125	4		
6 2 1	2.093	14	2.093	29	2.110	15	2.110	21
0 4 3	2.092	14			2.110	15		
6 2 $\bar{5}$	2.092	14			2.111	15		
8 0 0	2.001	1	2.001	3	2.018	1	2.019	2
4 4 $\bar{4}$	2.000	2			2.019	2		
2 0 4	1.983	2	1.988	7	1.995	2	1.995	4
1 1 $\bar{5}$	1.983	4			1.995	5		
5 5 $\bar{1}$	1.921	10	1.921	11	1.941	11	1.939	4
10 0 $\bar{4}$	1.920	4			1.941	5		
4 2 3	1.875	3	1.873	10	1.887	4	1.887	10
1 3 4	1.874	3			1.888	3		
5 1 $\bar{6}$	1.874	3			1.888	3		
10 0 $\bar{2}$	1.870	4			1.889	4		
5 5 $\bar{3}$	1.870	6			1.889	7		
5 3 2	1.861	3			1.876	3	1.875	5
2 4 3	1.861	3			1.876	3		
7 1 $\bar{6}$	1.860	3			1.877	3		
9 3 $\bar{2}$	1.830	6	1.830	10	1.849	6	1.847	6
0 6 1	1.830	6			1.849	6		
9 3 $\bar{4}$	1.830	6			1.850	6		
10 2 $\bar{3}$	1.828	2			1.848	3		
2 6 $\bar{1}$	1.828	2			1.847	3		
8 4 $\bar{3}$	1.828	2			1.848	3		
3 1 4	1.791	2	1.798	9	1.802	2	1.804	3
0 2 5	1.791	2			1.802	2		
3 1 $\bar{6}$	1.791	2			1.803	2		
1 1 5	1.744	2	1.750	3	1.754	2	1.753	7
2 0 $\bar{6}$	1.744	1			1.754	1		
9 3 $\bar{1}$	1.735	6	1.738	13	1.752	6		
0 6 2	1.735	6			1.752	6		
9 3 $\bar{5}$	1.735	5			1.753	6		
5 5 1	1.701	2	1.700	4	1.717	2	1.718	2
10 0 $\bar{6}$	1.701	1			1.718	1		
6 6 $\bar{2}$	1.615	7			1.633	7	1.632	2
12 0 $\bar{4}$	1.615	4			1.633	4		
10 0 0	1.601	2			1.615	1	1.616	2
5 5 $\bar{5}$	1.600	4			1.615	3		
9 1 1	1.576	5	1.578	13	1.589	6	1.589	8
6 4 2	1.576	3			1.589	2		
3 5 3	1.576	3			1.589	2		
3 5 $\bar{5}$	1.576	5			1.590	6		
6 4 $\bar{6}$	1.576	5			1.590	6		
9 1 $\bar{7}$	1.576	3			1.590	2		
0 0 6	1.576	3			1.585	4		

[a] Using the LAZY-PULVERIX computer program,[13] both patterns were calculated from atomic coordinates of $CaSO_3\cdot 4H_2O$,[11] atomic occupancies and temperature factors as given in Table 2, and unit cell dimensions as given in Table 4 ($CaSO_3\cdot 4H_2O$, sample C).

[b] The $CaSO_3\cdot 4H_2O$ pattern has been reported by Shiino et al.[10] with rhombohedral indices. The $Ca_3(SO_3)_2SO_4\cdot 12H_2O$ pattern has been obtained by using CuKα radiation (λ = 1.5406 Å), scan speed 0.25 °(2Θ)/min and Si as an internal standard. Intensities were measured as peak-heights above background and expressed as a percentage of the strongest line.

(2) The dehydration temperature is substantially higher in $Ca_3(SO_3)_2SO_4\cdot12H_2O$ (e.g., in thermogravimetric analysis at a heating rate of 5 °C/min, 60 - 160 °C as against 30 - 69 °C in $CaSO_3\cdot4H_2O$ 8)).

(3) The heat of dehydration per mole of water lost, is larger in the double-salt by about one order of magnitude.15)

It should be noted that the solid solution range extends from pure $CaSO_3\cdot4H_2O$ to pure $Ca_3(SO_3)_2SO_4\cdot12H_2O$. Solid solutions of higher SO_4^{2-} content than that of $Ca_3(SO_3)_2SO_4\cdot12H_2O$ form a new type which will be discussed elsewhere. In addition, solid solutions of lower SO_4^{2-} content than that of sample A are unstable and partially decompose to $CaSO_3\cdot0.5H_2O$ at room temperature.

In conclusion, our results support the crystalline structure proposed by Matsuno et al.11) for $CaSO_3\cdot4H_2O$, and we propose this structure after minor alterations for the double-salt.

It is still possible that the dihydrate reported by early authors could be obtained in the presence of a contaminant prevalent 50-100 years ago and unknown to us. Alternatively we must assume that these early authors, duplicating each other's experiments, prepared the tetrahydrate and analyzed their product when dehydration to $CaSO_3\cdot0.5H_2O$ had progressed about half way.

Table 4. Calculated a) unit cell constants of samples A-D in comparison with $CaSO_3\cdot4H_2O$ dimensions

	$CaSO_3\cdot4H_2O$ b)	A c)	B c)	C c)	D c)
a(Å)	19.385(11)	19.578(2)	19.597(2)	19.594(2)	19.581(2)
b(Å)	11.192(4)	11.301(1)	11.318(1)	11.311(1)	11.307(1)
c(Å)	11.449(10)	11.518(1)	11.531(1)	11.539(2)	11.574(1)
β(°)	124.34(4)	124.51(1)	124.50(1)	124.51(1)	124.33(1)
V(Å^3)	2051 (2)	2100 (1)	2108 (1)	2107 (1)	2116 (1)

a) From 40 X-ray diffraction lines using the CELDM computer program for least-squares, estimated standard deviations given in parentheses.

b) Reported by Matsuno et al.11)

c) Mole ratio (SO_4^{2-}/Ca^{2+}): 0.260 for A, 0.294 for B, 0.332 for C and 0.378 for D.

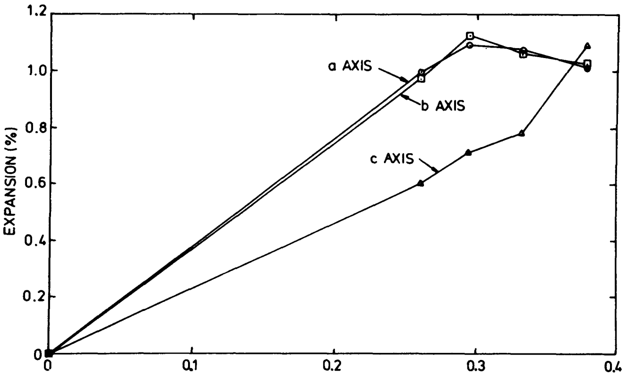

Fig. 1. Change in lattice parameters of $CaSO_3\cdot4H_2O$ obtained on substituting SO_3^{2-} with SO_4^{2-}.

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References

1) A. Cohen and M. Zangen, part IV of this series, submitted for publication.
2) A. Rohrig, J. Prakt. Chem., 37, 217 (1888).
3) F.R. Bichowsky, J. Am. Chem. Soc., 45, 2225 (1923).
4) F.W. Matthews and A.O. McIntosh, Can. J. Res., 26B, 747 (1948).
5) K. Setoyama, S. Takahashi, and M. Sekiya, Gypsum Lime, 141, 57 (1976).
6) A. Cohen, "New Crystalline Phases from Crystallographic, Thermal and Microscopic Studies of Alkaline Earth Sulfites," Ph.D Thesis, Bar-Ilan University, Ramat-Gan, Israel (1981),in Hebrew.
7) Attempts to prepare $Ca_3(SO_3)_2SO_4\cdot12H_2O$ by dropping a 100 ml of 1 M aqueous solution of $CaCl_2$ into a 100 ml of 1 M aqueous solution of Na_2SO_3 and Na_2SO_4 (mole ratio 2 : 1), or by simultaneous dropping of both solutions, yielded phases with low sulfate content, i.e. of mole ratio SO_4^{2-}/SO_3^{2-} being significantly lower than 0.5. This cannot only be attributed to a preference for the precipitation of calcium sulfite because of its lower solubility product, since a high concentration of Ca^{2+} and SO_4^{2-} ions (higher than five times the solubility of gypsum) remained in solution when simultaneous dropping of both solutions was performed. Hence the explanation of the phenomenon should be in terms of the formation of a stable supersaturated calcium sulfate solution and/or the formation of soluble complexes of calcium sulfate-calcium sulfite.1)
8) T. Matsuno and M. Koishi, Nippon Kagaku Kaishi, 1979, 1687 (1979).
9) M.T. McCall and M.E. Tadros, Colloids Surf., 1, 161 (1980).
10) H. Shiino, T. Yasue, and Y. Arai, Gypsum Lime, 180, 217 (1982).
11) T. Matsuno, H. Takayanagi, K. Furuhata, M. Koishi, and H. Ogura, Chem. Lett., 1983, 459 (1983).
12) J.W. Visser, J. Appl. Cryst., 2, 89 (1969).
13) K. Yvon, W. Jeitschko, and E. Parthe, J. Appl. Cryst., 10, 73 (1977).
14) Note the remarkable difference - the intensity ratio of the diffraction planes $\{11\bar{1}\}/\{111\}$ is 1.27 and 0.66 in $CaSO_3\cdot4H_2O$ and $Ca_3(SO_3)_2SO_4\cdot12H_2O$,respectively.
15) A. Cohen and M. Zangen, results to be published.

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