Studies on Alkaline-earth Metal Sulphites. Part 9.[1] Solid Solutions of $Ca_3(SO_4)_2SO_3{\cdot}12H_2O$ in $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$: Structure, Stability, and Dehydration Products

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Results of chemical and thermal analyses and of *X*-ray powder diffraction measurements show the instability of the expected compound, $Ca_3(SO_4)_2SO_3{\cdot}12H_2O$ (**3**), homologous to $CaSO_3{\cdot}4H_2O$ (**1**) and $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$ (**2**). A solid solution of (**2**) and (**3**) containing up to *ca.* 0.25 mole fraction of (**3**) is stable and structurally similar to (**2**) and (**1**). A crystallographic structure is proposed for this solid solution. The factors contributing to the stability of the highly hydrated compounds (**1**)—(**3**), and their solid solutions, are presented and discussed.

In a previous paper[2] we reported the existence of the double salt $Ca_3(SO_3)_2SO_4{\cdot}12H_2O$ (**2**) and of its solid solution in $CaSO_3{\cdot}4H_2O$ (**1**). In an additional paper,[3] we reported the location of the hydrogen atoms and the existence of a large number of hydrogen bonds in these highly hydrated salts. The thermal behaviour and stability of these compounds, and the nature of the products of their dehydration, were also investigated and reported.[1]

In the course of our research on the properties of (**2**), a number of experiments were performed in which the mole ratio $SO_4^{2-}:Ca^{2+}$ exceeded 1:3. The results of these experiments indicate the instability of the expected compound, $Ca_3(SO_4)_2SO_3{\cdot}12H_2O$ (**3**), but show the existence of its solid solution in (**2**). Data on these solid solutions are now presented, and the stability of compounds (**1**)—(**3**), and their solid solutions, is discussed.

Experimental

Sample Preparation.—Five samples (**A**—**E**) were prepared at 3—5 °C. Aqueous solutions (1 mol dm^{-3}, 100 cm^3), consisting of Na_2SO_3 and Na_2SO_4 in various ratios, were stirred into an aqueous solution of $CaCl_2$ (1 mol dm^{-3}, 100 cm^3). 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.

The products obtained were studied by chemical analysis, *X*-ray powder diffraction, and thermal analysis.

Chemical Analysis.—Sulphite was determined by iodometry, calcium by complexometry with ethylenediaminetetra-acetate using methylthymol blue as indicator, and water by thermogravimetry. The sulphate content was calculated as the difference between calcium and sulphite values (in mole fraction). Argentimetry (Mohr procedure) showed the absence of chloride from the products, while flame spectroscopy tests showed the presence of sodium to be negligible.

Instrumentation.—A Rigaku D/Max-III *X*-ray powder diffractometer, a DuPont-1090 thermal analysis data system, a DuPont-910 differential scanning calorimeter, and a DuPont-951 thermogravimetric analyzer were employed in the experiments.

Results

Chemical Composition.—Chemical analyses of samples **A**—**E** (Table 1) show that their $SO_4^{2-}:Ca^{2+}$ mole ratios are 0.332, 0.378, 0.402, 0.443, and 0.541 respectively.

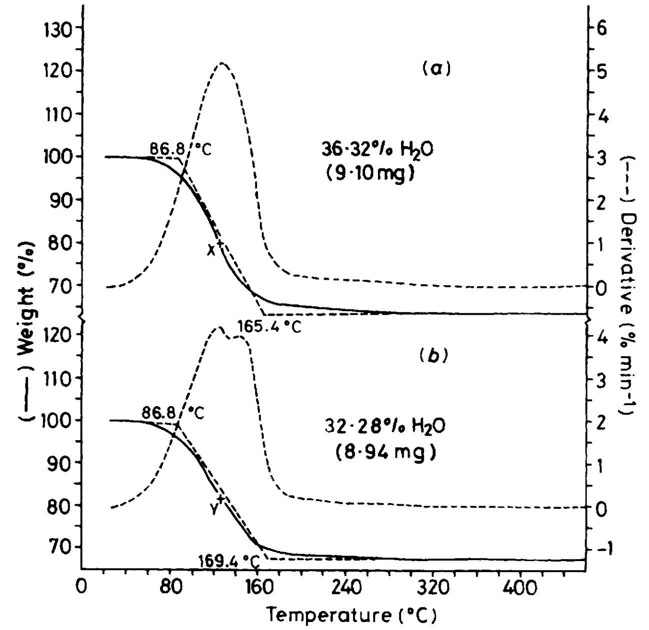

Figure. T.g.–d.t.g. curves for the dehydration of (*a*) sample **B**, (*b*) sample **E**. Heating rate, 10 °C min^{-1}; atmosphere, N_2 (50 cm^3 min^{-1}). Point X = 125.2 °C, Y = 128.0 °C

Thermal Analysis.—The thermogravimetric (t.g.) results are summarized in Table 1 and the Figure shows t.g. and d.t.g. (differential thermogravimetric) curves of samples **B** and **E** 2 weeks after their preparation. It can be seen that the $H_2O:Ca$ mole ratio is *ca.* 4, as in the compounds (**1**) and (**2**) previously studied. Dehydration temperatures and heats of dehydration are also very similar to those found for compound (**2**),[1] although there is a slight gradual decrease in dehydration temperatures with increasing sulphate content. In samples **D** and **E**, the d.t.g. curve shows a second dehydration peak near 140 °C. A somewhat lower water content is found for sample **E**, which was shown (see below) to contain appreciable amounts of $CaSO_4{\cdot}2H_2O$. After 2 weeks, both samples **D** and **E** show a significant decrease in water content.

Transition temperatures and heats of transition from differential scanning calorimetric (d.s.c.) measurements are given in Table 2. As expected, the endothermic transition (dehydration) temperatures obtained using an open pan, where

Table 1. Results of chemical and thermogravimetric[a] analyses[b] of $Ca_3(SO_3)_2SO_4\cdot12H_2O$–$Ca_3(SO_4)_2SO_3\cdot12H_2O$ solid solutions

	Composition (wt. %)[c]					Mole ratio		Dehydration temp. (°C)[d]	
Sample	CaO	SO_2	SO_3	H_2O	Total	SO_3:CaO	H_2O:CaO	T_o	T_p
A	28.3	21.6	13.4	36.5	99.8	0.332	4.01	89.7	129.5
B	28.1	20.0	15.2	36.3	99.6	0.378	4.02	86.8	127.0
C	28.3	19.3	16.2	35.8	99.6	0.402	3.94	84.1	122.8
D	28.7	18.2	18.1	34.5	99.5	0.443	3.75	84.8	123.2, 137
D′	28.1	17.9	17.8	35.8	99.6	0.443	3.97		
E	29.3	15.3	22.6	32.4	99.6	0.541	3.45	86.8	124.0, 145
E′	28.2	14.8	21.8	34.9	99.7	0.541	3.85		
e	28.39	21.62	13.51	36.48	100.00	0.3333	4.000		
f	28.01	16.00	20.00	35.99	100.00	0.5000	4.000		

[a] Performed at a heating rate of 10 °C min^{-1}. [b] All samples were analysed 2 weeks after their preparation during which period they were kept at 0 °C. Samples **D** and **E** were also analysed shortly after preparation (**D′** and **E′** respectively). [c] Estimated error ± 0.1%. [d] T_o = Extrapolated onset temperature (intersection of the slope and base lines); T_p = peak temperature; estimated errors ±0.5 °C. [e] Theoretical values for $Ca_3(SO_3)_2SO_4\cdot12H_2O$. [f] Theoretical values for $Ca_3(SO_3)_{1.5}(SO_4)_{1.5}\cdot12H_2O$.

Table 2. Transition temperatures[a] (°C) and heats of transition[b] (J g^{-1}) of the mixed salts from differential scanning calorimetric analysis[c]

	Mole ratio SO_4^{2-}:Ca^{2+}	T_o	T_p	ΔH_1	T_o	T_p	ΔH_2
Sample in an open pan							
A	0.332	70.5	107.0	−885	323.6	347.0	+34.9
B	0.378	65.0	96.1	−920	341.8	357.0	+56.0
C	0.402	65.4	101.7	−880	328.2	349.2	+48.5
Sample in a closed pan							
A	0.332	128.4	153.8	−956	331.6	346.4	+38.0
B	0.378	127.8	158.4	−886	335.3	359.6	+47.5
C	0.402	127.4	154.8	−900	333.5	354.2	+32.6

[a] T_o = Extrapolated onset temperature; T_p = peak temperature; estimated errors ±0.5 °C. [b] Each sample underwent two transitions, the heats of which are given by ΔH_1 and ΔH_2; $\Delta H > 0$, exothermic transition; $\Delta H < 0$, endothermic transition; estimated error ±5%. [c] Performed at a heating rate of 5 °C min^{-1}.

any water vapour is immediately removed by a stream of dry nitrogen, are much lower (by *ca.* 50 °C) than those obtained in a closed pan under increased water vapour pressure. Such a difference is of course not observed in the exothermic transition around 350 °C, which is merely a recrystallization of the anhydride.[1]

X-Ray Powder Diffraction Analysis.—The *X*-ray powder diffraction patterns of samples **A**—**E** were measured. The patterns of samples **A**, **C**, and **E** are compared in Table 3 to the calculated pattern of $Ca_3(SO_3)_2SO_4\cdot12H_2O$ (**2**). It can be seen that, for samples of SO_4^{2-}:Ca^{2+} mole ratio up to 0.40, the diffraction pattern is very similar to that of (**1**) and (**2**),[2] although the unit-cell shows a slight expansion (Table 4). At higher sulphate content several new diffraction lines appear, with total retention of the (slightly displaced) lines of the previous pattern. The slightly modified structure indicated by these lines is, however, not stable enough to allow independent accurate determination. Upon gradual disappearance of the new lines, complete within 1 week, the lines characteristic of $CaSO_4\cdot2H_2O$ appear. In sample **E**, unlike sample **D**, some of these latter lines are already present when the sample is first submitted to *X*-ray diffractometry (shortly after preparation), but grow considerably stronger as time passes.

The *X*-ray powder diffraction patterns of the anhydrides of samples **A**—**E** were measured. All samples show the same diffraction pattern as the anhydride $Ca_3(SO_3)_2SO_4$ (**1′**).[1] The unit-cell dimensions of the anhydrides of samples **A**—**C** (**A′**—**C′**, obtained upon dehydrating samples **A**—**C** to 500 °C in an inert atmosphere) were calculated from their respective diffraction patterns and are presented in Table 5.

Discussion

A study of the crystalline structure of $CaSO_3\cdot4H_2O$ (**1**)[4] and $Ca_3(SO_3)_2SO_4\cdot12H_2O$ (**2**)[2] shows that, potentially, the mixed salt $Ca_3(SO_4)_2SO_3\cdot12H_2O$ (**3**) could exist in the same structure. In addition to the $S(2)O_3^{2-}$ groups of (**1**)[4] being replaced with $S(2)O_4^{2-}$ groups in (**2**),[2] half the $S(1)O_3^{2-}$ could, in theory, be similarly replaced without substantially straining the crystalline structure. The only changes necessitated by the latter replacement would be the following.

(*a*) There would be a shortening of the S(1)–O(1), S(1)–O(2), and S(1)–O(3) bonds[5] from an average of 1.527(6) Å, as in SO_3^{2-}, to an average of 1.434(8) Å, as in SO_4^{2-}.[5] If these oxygen atoms, belonging to the co-ordination sphere of calcium ions, are assumed to remain in place, the S(1) atom would have to be slightly displaced.

(*b*) The addition of an oxygen atom in a new site, O(14), is required, yielding a tetrahedral symmetry with O(1), O(2), and O(3) around S(1). Provided this happens only in half the $S(1)O_3^{2-}$ groups, *i.e.* occupancy of 0.5 for O(14), the new oxygens need not interfere with the O(4) atoms. There is also no interference with any other atom in the structure, except slightly with S(2).

(*c*) Each $S(2)O_4^{2-}$ group would be limited to a single orientation, instead of the two orientations available in (**2**)[2] and the six orientations available in (**1**),[4] in order to avoid interference between O(4) and O(14).

Table 3. *X*-Ray powder diffraction patterns[a] of samples **A**, **C**, and **E**[b] compared to the calculated[c] pattern of $Ca_3(SO_3)_2SO_4\cdot12H_2O$

$Ca_3(SO_3)_2SO_4\cdot12H_2O$					Sample **A**		Sample **C**		Sample **E**	
h	*k*	*l*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
1	1	−1	8.0760	66	8.0786	44	8.1469	35	8.1424	28
2	0	0	8.0730	33						
									7.6159^d	8
2	0	−2	5.7674	51	5.7696	100	5.8178	100	5.9089	100
1	1	1	5.7645	100						
3	1	−1	5.6561	79	5.6514	31	5.6719	18	5.7748	28
0	2	0	5.6555	40						
									5.6182	18
3	1	−2	4.8623	9	4.8630	16	4.8774	12	4.8739	15
0	2	1	4.8607	10						
3	1	0	4.8599	9						
4	0	−2	4.6338	9	4.6309	11	4.6432	7	4.6159	5
2	2	0	4.6320	16						
									4.2808^d	14
2	2	−2	4.0380	1	4.0437	2	4.0600	2		
4	0	0	4.0365	1						
									3.8011^d	4
5	1	−2	3.6723	8	3.6689	14				
4	2	−1	3.6717	8						
1	3	0	3.6716	8						
3	1	−3	3.6403	35	3.6391	67	3.6624	74	3.7164	78
0	2	2	3.6392	35						
3	1	1	3.6384	35						
									3.6414	23
6	0	−2	3.2657	18	3.2627	19	3.2672	12	3.2729	5
3	3	−1	3.2653	35						
									3.2299	12
4	2	−3	3.1066	11	3.1075	19	3.1165	17	3.1190	20
1	3	−2	2.1059	11						
5	1	0	3.1051	11						
									3.0651^d	
										13
4	0	−4	2.8837	11	2.8824	23	2.9010	24	2.9555	25
2	2	2	2.8823	23						
5	1	−4	2.7413	14	2.7418	27	2.7528	27	2.8620	17
1	3	2	2.7401	15					2.7769	25
4	2	1	2.7397	14						
									2.7435	9
6	0	−4	2.6926	14	2.6930	63	2.6997	50	2.7062	43
3	3	−3	2.6920	46						
3	3	1	2.6912	28						
6	0	0	2.6910	23						
									2.5417	16
									2.4921	23
7	1	−4	2.4537	6			2.4771	8		
2	4	1	2.4527	7	2.4533	12	2.4581	11	2.4532	12
5	3	0	2.4526	7						
6	2	−4	2.4311	2	2.4318	3	2.4362	5		
0	4	2	2.4303	2						
6	2	0	2.4299	2						
0	0	4	2.3771	17	2.3749	9	2.3973	13	2.3705	5
5	3	−4	2.2611	5	2.2614	7	2.2679	6	2.2727	5
2	4	−3	2.2607	5						
7	1	0	2.2601	5						
8	2	−3	2.2407	7	2.2387	5	2.2404	3		
7	3	−2	2.2404	6						
1	5	0	2.2403	6						
7	3	−3	2.2203	3	2.2194	3	2.2210	2		
8	2	−2	2.2199	3						
1	5	−1	2.2199	3						
									2.2164^d	4
									2.1820	11

Table 3 (*continued*)

$Ca_3(SO_3)_2SO_4{\cdot}12H_2O$					Sample A		Sample C		Sample E	
h	*k*	*l*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
8	2	−4	2.1440	3						
1	5	1	2.1433	3	2.1420	7				
7	3	−1	2.1432	3						
9	1	−3	2.1379	4						
6	4	−2	2.1377	3	2.1380	8				
3	5	−1	2.1376	4						
4	2	−5	2.1246	4						
1	3	−4	2.1242	5	2.1220	10				
5	1	2	2.1235	5						
6	2	−5	2.1107	15						
0	4	3	2.1100	15	2.1103	21	2.1188	20	2.1371	21
6	2	1	2.1096	15						
									2.1123	9
4	4	−4	2.0190	2	2.0191	2	2.0209	4	2.0835	5
8	0	0	2.0182	1						
1	1	−5	1.9950	5	1.9949	4	2.0081	4		
2	0	4	1.9946	2						
									1.9909[d]	2
10	0	−4	1.9413	5	1.9391	4	1.9390	3	1.9459	11
5	5	−1	1.9409	11						
5	5	−3	1.8893	7						
10	0	−2	1.8891	4						
5	1	−6	1.8882	3	1.8869	10	1.8905	6	1.9089	5
1	3	4	1.8875	3						
4	2	3	1.8873	4						
7	1	−6	1.8766	3						
2	4	3	1.8757	3	1.8750	5			1.8775	11
5	3	2	1.8755	3						
9	3	−4	1.8496	6						
0	6	1	1.8492	6						
9	3	−2	1.8492	6	1.8470	6	1.8486	4		
8	4	−3	1.8475	3						
10	2	−3	1.8475	3						
2	6	−1	1.8473	3						
									1.8328	11
									1.8123[d]	4
3	1	−6	1.8028	2						
0	2	5	1.8025	2	1.8037	3	1.8164	4		
3	1	4	1.8022	2						
									1.7787[d]	2
2	0	−6	1.7542	1						
1	1	5	1.7539	2						
9	3	−5	1.7529	6	1.7525	7	1.7549	5	1.7461	7
0	6	2	1.7524	6						
9	3	−1	1.7523	6						
10	0	−6	1.7177	1	1.7176	2	1.7185	2		
5	5	1	1.7168	2						
									1.6620	7
									1.6111	8
9	1	−7	1.5901	2						
6	4	−6	1.5898	6						
3	5	−5	1.5896	6	1.5894	8	1.5949	7	1.5892	4
3	5	3	1.5893	2						
6	4	2	1.5892	2						
9	1	1	1.5891	6						

[a] Obtained by using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å). Scan speed 0.25° (2θ) min^{-1} with elemental Si as internal standard. *d* Values were determined at 80% of peak intensity. Intensities were measured as peak heights above background and are expressed as a percentage of the strongest line. [b] Mole ratio SO_4^{2-} : Ca^{2+} of samples is 0.332, 0.402, and 0.541 respectively. [c] Using the LAZY-PULVERIX computer program (K. Yvon, W. Jeitschko, and E. Parthe, *J. Appl. Cryst.*, 1977, **10**, 73) calculated from atomic co-ordinates of $CaSO_3{\cdot}4H_2O$,[4] and atomic occupancies, thermal parameters and unit-cell dimensions as reported by Cohen and Zangen.[2] The calculated pattern shows many groups of 2—6 diffraction lines close together and unresolved in the observed pattern. For least-squares calculations of unit-cell constants (Table 4), the observed lines were attributed to the strongest lines in the groups. This was done only where the intensity of the latter was twice that of the others in the corresponding groups. [d] *X*-Ray diffraction line characteristic of $CaSO_4{\cdot}2H_2O$.

Table 4. Calculated unit-cell constants* of samples A—D (monoclinic, space group *C*2/*c*)

Sample	A	B	C	D
a/Å	19.594(2)	19.593(6)	19.584(6)	19.538(6)
b/Å	11.311(1)	11.320(4)	11.318(5)	11.291(5)
c/Å	11.539(2)	11.570(3)	11.613(5)	11.670(4)
β/°	124.51(1)	124.34(2)	124.18(3)	123.90(3)
U/Å^3	2 107(1)	2 119(1)	2 129(1)	2 137(1)
Mole ratio SO_4^{2-}:Ca^{2+}	0.332	0.378	0.402	0.443

* Calculated using a least-squares computer program (D. E. Appleman, H. T. Evans, and D. S. Handwerker, Indexing and Least-squares Refinement of Powder Diffraction Data, Geological Survey, Washington, 1973, distributed by National Technical Information Service, Springfield, document no. PB-216188). Estimated standard deviations are given in parentheses.

Table 5. Calculated unit-cell constants* of the anhydrides of samples A—C

Sample	A′	B′	C′
a/Å	6.467(1)	6.470(2)	6.492(1)
b/Å	6.725(1)	6.723(2)	6.728(1)
c/Å	6.420(1)	6.422(1)	6.413(1)
β/°	102.92(1)	102.97(2)	103.10(1)
U/Å^3	272.12(4)	272.20(9)	272.85(4)
Mole ratio SO_4^{2-}:Ca^{2+}	0.332	0.378	0.402

* See footnote to Table 4. The anhydrides were obtained by thermal dehydration to 500 °C, in an inert atmosphere, of samples **A**, **B**, and **C** respectively.

Table 6. Postulated atomic co-ordinates of $Ca_3(SO_4)_{1.25}(SO_3)_{1.75}$·$12H_2O$ (monoclinic, space group *C*2/*c*)

Atom	Occupancy	Atoms in unit cell	*x*	*y*	*z*	Remarks
Ca(1)	1	4	0.0000	0.0440	0.2500	*a*
Ca(2)	1	8	0.1031	0.3530	0.2502	*a*
S(1)	0.875	7	0.0771	0.2500	0.4813	*b*
S(2)	1	4	0.2500	0.2500	0.0000	*a*
S(3)	0.125	1	0.0680	0.2500	0.4542	*c*
O(1)	1	8	−0.0081	0.1885	0.4112	*a*
O(2)	1	8	0.1152	0.1890	0.4116	*a*
O(3)	1	8	0.0533	0.3725	0.4106	*a*
O(4)	0.5	4	0.2002	0.2492	−0.1519	*a*
O(5)	0.5	4	0.2334	0.1597	0.0688	*a*
O(6)	0.5	4	0.3384	0.2376	0.0673	*a*
O(7)	0.5	4	0.2501	0.3583	0.0681	*a*
O(8)	1	8	0.0694	0.0891	−0.0540	*a*
O(9)	1	8	0.1138	0.0288	0.7346	*a*
O(10)	1	8	0.0745	0.4321	0.7336	*a*
O(11)	1	8	0.1056	0.4126	0.0534	*a*
O(12)	1	8	0.2042	0.2114	0.2653	*a*
O(13)	1	8	0.2674	0.0749	0.5529	*a*
O(14)	0.125	1	0.1189	0.2500	0.6059	*c*
H(1)	0.5	4	0.130	0.115	−0.008	*d*
H(2)	0.5	4	0.103	0.153	−0.059	*d*
H(3)	1	8	0.047	0.126	−0.001	*d*
H(4)	0.5	4	0.146	0.110	−0.223	*d*
H(5)	0.4375	3.5	0.164	0.071	−0.192	*e*
H(6)	1	8	0.141	−0.015	−0.300	*d*
H(7)	0.5	4	0.121	0.364	−0.224	*d*
H(8)	0.4375	3.5	0.107	0.369	−0.193	*e*
H(9)	1	8	0.022	0.397	−0.300	*d*
H(10)	0.5	4	0.126	0.357	0.009	*d*
H(11)	0.5	4	0.159	0.392	0.059	*d*
H(12)	1	8	0.086	0.492	0.001	*d*
H(13)	0.5	4	0.240	0.226	0.223	*d*
H(14)	0.4375	3.5	0.215	0.192	0.192	*e*
H(15)	1	8	0.213	0.132	0.300	*d*
H(16)	0.5	4	0.255	0.012	0.059	*d*
H(17)	0.5	4	0.261	0.005	0.008	*d*
H(18)	1	8	0.211	−0.117	0.001	*d*
H(19)	0.0625	0.5	0.116	0.111	−0.313	*c*
H(20)	0.0625	0.5	0.091	0.365	−0.314	*c*
H(21)	0.0625	0.5	0.270	0.226	0.313	*c*

[a] From ref. 4. [b] From ref. 4, but with occupancy 0.875 instead of 1. [c] Calculated in this paper. [d] From ref. 3. [e] From ref. 3, but with occupancy 0.4375 instead of 0.5.

It should be noted that H(19), H(20), and H(21) replace H(5), H(8), and H(14) respectively, since they cannot coexist, the angles H(19)–O(9)–H(5), H(20)–O(10)–H(8), and H(21)–O(12)–H(14) being *ca.* 73°. The hydrogen atoms H(6), H(9), and H(15), therefore, remain uninvolved in hydrogen bonds as in the previously studied compounds.[3]

(*d*) A slight increase in the S(1)–S(2) distance would occur, additional to that already obtained by displacement of S(1), in order to eliminate any interference between O(14) and S(2). This is in fact obtained by the observed increase in dimension *c* and decrease in angle β, as shown in Table 4.

(*e*) Additional alternative sites for the hydrogen atoms bound to O(9), O(10), and O(12) are required, in order to provide hydrogen bonds for O(14), since this oxygen atom is not within bond-forming distance of any Ca atom. [Like O(4), O(5), O(6), and O(7), we should expect O(14) to participate in three hydrogen bonds,[3] and the water oxygens O(9), O(10), and O(12) are at the appropriate distance.]

Atomic co-ordinates for the expected structure of $Ca_3(SO_4)_2SO_3\cdot12H_2O$, calculated to comply with the above requirements, are given in Table 6. Since, however, this structure appears to exist only in solid solutions where the SO_4^{2-}: Ca^{2+} mole ratio is $\leqslant 0.40$ the 'occupancy' and 'number of atoms' columns in Table 6 show the values for $Ca_3(SO_4)_{1.25}(SO_3)_{1.75}\cdot12H_2O$ (approximately sample **C**).

The following questions now arise. If the previously studied crystalline structure can so easily accommodate the additional oxygen, O(14), why should $Ca_3(SO_4)_2SO_3\cdot12H_2O$ be so unstable compared to $Ca_3(SO_3)_2SO_4\cdot12H_2O$? Why is the former double salt only stabilized in solid solutions with the latter where the $SO_4^{2-}:Ca^{2+}$ mole ratio does not exceed 0.40, while any additional sulphate is, within a short time, converted into $CaSO_4\cdot2H_2O$? A study of the factors contributing to the stability of the highly hydrated compounds (**1**)—(**3**) (the same arguments may apply to other highly hydrated salts) may provide the answer to the above questions. These factors are as follows: (i) maximal hydrogen bonding of oxygens, especially those O atoms not participating in the co-ordination sphere of the Ca atoms;[3] (ii) maximal participation of H atoms in hydrogen bonds;[2,3] and (iii) minimal disorder in the crystallographic unit cell.[2]

Comparing compounds (**1**) and (**2**), we can see that in both cases, factor (i) is satisfied. Participation of hydrogen atoms in H-bonding is, however, higher by 20% in (**2**),[2,3] and the disorder of oxygen atoms around S(2) is decreased at least by a factor of three.[2] This explains the large increase in stability of $Ca_3(SO_3)_2SO_4\cdot12H_2O$ over $CaSO_3\cdot4H_2O$.[2] However, if compound (**3**) is compared to (**2**), it can be seen that factor (ii) is unchanged. On the other hand, factor (iii) is improved in (**3**) as far as individual $S(2)O_4^{2-}$ groups are concerned (short-range order), but the overall (long-range) disorder now includes the S(1) atom as well as the $S(2)O_4^{2-}$ oxygens. However, factor (i) in particular is no longer satisfied in $Ca_3(SO_4)_2SO_3\cdot12H_2O$, because O(5), O(6), and O(7) now compete with O(14) for the same hydrogen atoms [locations H(5), H(8), and H(14) or locations H(19), H(20), and H(21)]. This competition results in an average of 2.5 hydrogen bonds instead of three for O(5), O(6), and O(7), and an average of only 1.5 hydrogen bonds instead of three for O(14). This may be the reason why only a limited fraction of $S(1)O_4^{2-}$ can be introduced into the structure, and a modified crystalline structure is sought when the $SO_4^{2-}:Ca^{2+}$ mole ratio exceeds 0.40.

The modified structure might be the result of a distortion whereby the hydrogen atoms H(6), H(9), and H(15) occupy sites which enable them to participate in hydrogen bonding, unlike the case in the structure of compounds (**1**) and (**2**).[3] Such a distortion may account for the new lines appearing especially near *d*-values which, in the original pattern, were associated with more than one *hkl*. Evidence of the resulting strain is shown in the increased changes in unit-cell dimensions between samples **C** and **D** (Table 4), and in the fact that the modified structure, whatever its form, is not stable either. This can be seen from the spontaneous formation of $CaSO_4\cdot2H_2O$ in samples **D** and **E**, as shown both by *X*-ray powder diffraction (Table 3) and by the double dehydration peak in thermogravimetry (Table 1).

The detailed crystalline structure of the mixed anhydrides, different from any known phase of $CaSO_3$ or $CaSO_4$, has not yet been determined. However, it may be seen that, as expected, the unit-cell dimensions increase with the increase in sulphate content (Table 5).

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