Structure and Properties of Calcium Sulfate Sulfite Dodecahydrate

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The crystal structure of $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$ was solved in the rhombohedric space group $R\bar{3}c$ with cell constants $a = 11.340(2)$ and $c = 28.056(5)$ Å. The structure was refined to $R = 0.023$ for 519 observed reflections. A disorder of 1:1 was found for the SO_4^{2-} anion placed on the inverse three-fold axis. The disorder is present even when a trial was made to refine the structure in lower-symmetry space groups. Both the sulfite and the sulfate anions are placed on a three-fold axis. The Ca^{2+} cation is located on a two-fold axis with a coordination number of eight. The hydrogen atoms of the water molecules were localized, and a three-dimensional hydrogen bond net is described.

It is well known that sulfur dioxide contributes to the deterioration of calcitic building stone. The end-product of the sulfation process is gypsum, $CaSO_4 \cdot 2H_2O$. Calcium sulfite hemihydrate, $CaSO_3 \cdot 0.5H_2O$, has been shown to be an intermediate in calcareous stone corrosion.[1,2] The formation of $CaSO_3 \cdot 0.5H_2O$ during the corrosion process triggers the question of whether other calcium sulfites may also play a role.

Calcium sulfite crystallizes from aqueous solution in the form of the hemihydrate $CaSO_3 \cdot 0.5H_2O$. Three modifications of the hemihydrate have been described: α-, β- and γ-$CaSO_3 \cdot 0.5H_2O$.[3] Anhydrous $CaSO_3$ is formed in an inert atmosphere during the dehydration of $CaSO_3 \cdot 0.5H_2O$ at 300–400 °C.[4] Two modifications of the anhydrate have been shown to exist.[5] A dihydrate, $CaSO_3 \cdot 2H_2O$, was reported in the older literature,[6] but has not been confirmed by later studies.[3,7–9]

In recent years a tetrahydrate, $CaSO_3 \cdot 4H_2O$, has been reported.[10–14] The tetrahydrate was found to crystallize in the presence of small amounts of sodium citrate at 4–10 °C[10,12,13] or nitrilotris(methylene)triphosphonic acid at 25 °C.[11] Ambiguous crystallographic data have defined the unit cell of the tetrahydrate as rhombohedral[12] or monoclinic.[13,14]

A double salt, $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$, and its solid solution in $CaSO_3 \cdot 4H_2O$ were prepared without the aid of additives at 3–5 °C.[15] The authors report the compound to be monoclinic.

Owing to the ambiguous crystallographic data, our work aimed to repeat earlier authors' syntheses of both $CaSO_3 \cdot 4H_2O$ and $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$. It was hoped that further crystallographic studies of these compounds would elucidate their structures.

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Experimental

Preparation of $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$. The preparative methods described by McCall and Tadros[11] for the synthesis of presumptive $CaSO_3 \cdot 4H_2O$ and by Cohen and Zangen[15] for the preparation of $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$ were employed with some modifications. All chemicals were of analytical reagent grade unless otherwise specified. In all preparations air was excluded from the system in order to avoid oxidation of the sulfite by molecular oxygen. Hydrogen peroxide was added in order to form a known amount of sulfate in the solution.

(i) Precipitation from hydrogen sulfite solution with the addition of nitrilotris(methylene)triphosphonic acid (NTMP) (single crystal preparation) was carried out according to reaction (1). A slurry consisting of approxi-

$$3Ca^{2+} + 4HSO_3^- + 10H_2O + SO_4^{2-} \rightarrow$$

$$Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O(s) + 2SO_2(g) \tag{1}$$
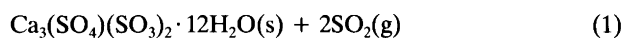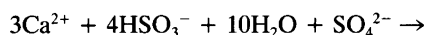
mately 5 g $CaCO_3$ in 175 ml high-purity water with the addition of 1 ml 50 wt% NTMP was degassed with $N_2(g)$ at ca. 100 ml min^{-1} in a three-necked round flask at 22 °C. $SO_2(g)$ was thereafter bubbled into the slurry together with $N_2(g)$ until the carbonate had completely dissolved at pH 2.5. The acidity of the solution was then adjusted to pH 3.0 by bubbling with $N_2(g)$. Then 0.40 M $H_2O_2(aq)$ was added producing SO_4^{2-} in the solution, corresponding to a Ca^{2+}: SO_4^{2-} ratio of 3:1. The pH was then adjusted to 4.0 with $N_2(g)$. The N_2-stream was halted, the crystallization vessel closed, and crystals formed within hours. The resulting precipitate was washed with high-purity, oxygen-free water and dried on a Buchner filter. The salt was stored at 2 °C. The crystals exhibited the same morphology as described by Shiino *et al.*[12] for $CaSO_3 \cdot 4H_2O$. Colourless block crys-

tals separated from the precipitate were utilized for structural and infrared investigations.

(ii) Metathesis from CaCl$_2$ and NaSO$_3$ solutions with the addition of nitrilotris(methylene)triphosphonic acid (NTMP) was carried out according to reaction (2). So-

$$3Ca^{2+} + 2SO_3^{2-} + SO_4^{2-} + 12H_2O \rightarrow$$

$$Ca_3(SO_4)(SO_3)_2\cdot 12H_2O(s) \qquad (2)$$
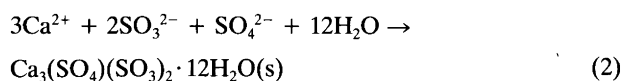
lutions consisting of 1.00 M CaCl$_2$(aq) and 1.00 M Na$_2$-(SO$_3$)$_{1-x}$(SO$_4$)$_x$)(aq) were prepared with N$_2$-degassed high-purity solutions obtained by the addition of 0.40 M H$_2$O$_2$ (aq) (prepared as the reagent solutions) to the Na$_2$SO$_3$(aq) solutions.

Approximately five drops of 50 wt% NTMP were added to the CaCl$_2$(aq) solutions. The mixtures were degassed with N$_2$ for ca. 5 min before addition of the Na$_2$SO$_3$/SO$_4$ (aq) solutions to a slight excess of CaCl$_2$(aq). Within minutes a precipitate formed which was then filtered and washed on a Buchner filter with N$_2$-degassed high-purity water and dried under nitrogen. Ca^{2+}:SO$_4^{2-}$ ratios from 3:1 to 3:2 produced the double salt. The powders were stored at 2 °C for later analyses.

(iii) In the case of preparation at 2–4 °C, identical synthesis procedures were implemented as under (ii) with the exception that NTMP was not added and all solutions were cooled to 2–4 °C. Ca^{2+}:SO$_4^{2-}$ ratios from 3:1 to 3:2.5 produced the double salt.

Procedures (ii) and (iii) produced Ca$_3$(SO$_4$)(SO$_3$)$_2$-·12H$_2$O only when the Na$_2$SO$_3$/SO$_4$(aq) mixture was poured into the CaCl$_2$(aq) solution and not *vice versa*. In the latter case a mixture of α-CaSO$_3$·0.5H$_2$O and gypsum was obtained.

Chemical analyses. A number of samples prepared using methods (i)–(iii) were analyzed. The analytical results given are for a sample produced using method (iii) at a Ca^{2+}:SO$_4^{2-}$ solution ratio of 3:1. *Found*: Ca^{2+} 20.8; S$_{tot}$ 16.4; SO$_3^{2-}$ 27.8; SO$_4^{2-}$ 15.8; H$_2$O 35.6. *Calc. for Ca$_3$(SO$_4$)-(SO$_3$)$_2$·12H$_2$O*: Ca^{2+} 20.3; S$_{tot}$ 16.2; SO$_3^{2-}$ 27.0; SO$_4^{2-}$ 16.2; H$_2$O 36.5.

Calcium was determined by complexometric titration with EDTA. Sulfite was analyzed by iodimetry. The total amount of sulfur was determined by ion chromatography (RP-IPC) after dissolution of the salt in several ml of 0.40 M H$_2$O$_2$(aq). Sulfate was calculated from the determinations of total sulfur and sulfite. Water was calculated from the determinations of calcium, sulfite and sulfate.

No evidence of solid solubility was found. However, in the course of the chemical analyses, a new compound with the composition Ca$_3$(SO$_4$)$_{1.5}$(SO$_3$)$_{1.5}$·12H$_2$O was found in samples prepared by methods (ii) and (iii). Further chemical and structural information on this compound will be published later.

Thermogravimetric analyses. Powders of Ca$_3$(SO$_4$)(SO$_3$)$_2$-·12H$_2$O weighing ca. 100 mg were placed in an open cruci-

ble. Both the balance housing and sample were constantly purged with nitrogen gas at 10 l h^{-1}. The samples were heated from 25 to 500 °C at a rate of 6 °C min^{-1}. The composition of the samples after thermal analysis was confirmed using X-ray powder diffraction.

The compound was found to decompose in the region of ca. 40–100 °C, forming calcium sulfate dihydrate and calcium sulfite hemihydrate. In the region of ca. 120–200 °C gypsum dehydrated to form calcium sulfate hemihydrate and later calcium sulfate anhydrate. Calcium sulfite hemihydrate dehydrated at ca. 400 °C, forming the anhydrate. Thus the major water loss occurred in the region of ca. 40–250 °C, and complete dehydration of the compound occurred at ca. 400 °C.

X-Ray powder diffraction analyses. All samples prepared by methods (i)–(iii) were examined by XRD. They were ground to a fine powder in an agate mortar and then lightly brushed on to adhesive tape. Silicon was used as internal standard. The instrument employed was a Guinier–Hägg camera with a rotating specimen holder. Film intensities were measured by an optical scanner (LS-20), and the resulting data were processed using the computer program SCANPI7.[16] The powder diffraction data for Ca$_3$(SO$_4$)-(SO$_3$)$_2$·12H$_2$O have been submitted to the JCPDS file system.

Infrared spectrum. The spectrum of Ca$_3$(SO$_4$)(SO$_3$)$_2$-·12H$_2$O was recorded on a Mattson Polaris FTIR spectrometer using the KBr disc method. Characteristic bands for SO$_3^{2-}$ were recorded at 948 cm^{-1} and for SO$_4^{2-}$ at 1112 cm^{-1}.

Crystal structure determination. A colourless crystal prepared by method (i), consisting of Ca$_3$(SO$_4$)(SO$_3$)$_2$·12H$_2$O measuring *ca.* 0.3×0.2×0.15 mm, was mounted on a glass fibre. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo K_α radiation and a 12 kW rotating anode generator. The data were collected at a temperature of −120±1 °C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Scans of (1.47 + 0.30 tan θ)° were made at a speed of 32.0° min^{-1} (in ω). The weak reflections [I<10.0 σ(I)] were rescanned (with a maximum of three rescans), and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Cell constants and an orientation matrix for data collection were obtained by least-squares refinement using the setting angles of 25 carefully centred reflections in the range 48.13 < 2θ < 49.28° and corresponded to a rhombohedral (hexagonal axes) cell of dimensions: a = 11.340(2), c = 28.056(5) Å, V = 3125(1) Å^3. At room temperature the cell constants were determined to a = 11.3514(6), c = 28.412(3) Å, V = 3170.6(5) Å^3. For Z = 6 and formula

Table 1. Positional parameters and B(eq) for $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$.

Atom	x	y	z	B(eq)^a/B
Ca	0	0.20294(6)	1/4	1.05(3)
S(1)	0	0	0.17191(3)	1.03(2)
O(1)	−0.1220(2)	−0.0002(2)	0.19570(6)	1.23(6)
S(2)	−1/3	1/3	1/3	1.29(4)
O(21)	−0.3877(4)	0.1934(3)	0.3119(1)	1.5(1)
O(22)	−1/3	1/3	0.3827(2)	1.7(1)
O(1W)	−0.2338(2)	0.1574(2)	0.24446(8)	2.04(7)
O(2W)	−0.0038(2)	0.3319(2)	0.31587(8)	2.55(8)
H(1)	−0.281(4)	0.106(4)	0.227(1)	4(1)
H(2)	−0.268(4)	0.191(3)	0.255(1)	3(1)
H(3)	−0.066(4)	0.334(4)	0.320(1)	5(1)
H(4)	0.063(4)	0.407(4)	0.326(1)	4.0(8)

$^a B_{eq} = (8/3)\pi^2 \Sigma_i \Sigma_j u_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 2. Intramolecular distances (in Å) for $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$.

Atom	Atom	Distance	Atom	Atom	Distance
Ca	Ca^{ii,iii}	3.985(2)	S(2)	O(21)$^{i,vii-xi}$	1.510(3)
Ca	S(1)^{i,iv}	3.177(1)	S(2)	O(22)^{i,vii}	1.386(6)
Ca	O(1)^{i,ii,v,vi}	2.520(2)	O(1W)	H(1)^i	0.75(3)
Ca	O(1W)^{i,v}	2.440(2)	O(1W)	H(2)^i	0.73(5)
Ca	O(2W)^{i,v}	2.371(3)	O(2W)	H(3)^i	0.73(5)
S(1)	O(1)$^{i-iii}$	1.535(3)	O(2W)	H(4)^i	0.86(3)

Symmetry codes:

(i)	x, y, z		(vii)	$-x-\frac{2}{3}, -y+\frac{2}{3}, -z+\frac{2}{3}$
(ii)	$-y, x-y, z$		(viii)	$-y, x-y+1, z$
(iii)	$-x+y, -x, z$		(ix)	$y-\frac{2}{3}, -x+y-\frac{1}{3}, -z+\frac{2}{3}$
(iv)	$y, x, -z+\frac{1}{2}$		(x)	$-x+y-1, -x, z$
(v)	$-x, -x+y, -z+\frac{1}{2}$		(xi)	$x-y+\frac{1}{3}, x+\frac{2}{3}, -z+\frac{2}{3}$
(vi)	$x-y, -y, -z+\frac{1}{2}$			

weight 592.60, the calculated density is 1.889 g cm^{-3}. The space group was determined to be $R\bar{3}(h)$ (No. 167).

Of the 1359 reflections which were collected, 723 were unique ($R_{int} = 0.022$). The intensities of three reflections measured after every 150 reflections remained constant, and no decay correction was applied. The linear absorption coefficient for Mo K_α is 11.6 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.94 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by a combination of Patterson and direct methods.[17] Hydrogen atoms were located on a difference Fourier map after isotropical refinement of non-hydrogen atoms and were refined isotropically. All non-hydrogen atoms were refined anisotrop-

ically. The final cycle of full-matrix least-squares refinement was based on 519 observed reflections and 66 variable parameters, and converged (the largest parameter shift was 0.01 times its e.s.d.) with unweighted and weighted agreement factors of $R = 0.023$ and $R_w = 0.026$ [eqn. (3)].

$$R_w = [(\Sigma \, w \, (|F_o| - |F_c|)^2 / \Sigma \, w \, F_o^2)]^{1/2} \qquad (3)$$

The standard deviation of an observation of unit weight was 1.33. The weighting scheme was based on counting statistics and included a factor ($p = 0.02$) to reduce the weight of the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to −0.37 and 0.21 e Å^{-3}, respectively.

Table 3. Intramolecular bond angles (°) for $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O^a$

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Ca^{ii}	Ca	Ca^{iii}	60.00	O(1)^{vi}	Ca	O(1)^{vi}	128.36(7)
O(1)^i	Ca	O(1)^{iii}	56.73(7)	O(1)^{vi}	Ca	O(2W)^i	85.47(7)
O(1)^i	Ca	O(1)^v	100.48(8)	O(1)^{vi}	Ca	O(2W)^v	151.54(6)
O(1)^i	Ca	O(1)^{vi}	74.41(6)	O(1W)^i	Ca	O(1W)^v	141.21(7)
O(1)^i	Ca	O(1W)^i	74.13(8)	O(1W)^i	Ca	O(2W)^i	75.95(8)
O(1)^i	Ca	O(1W)^v	134.27(6)	O(1W)^i	Ca	O(2W)^v	75.95(8)
O(1)^i	Ca	O(2W)^i	149.78(7)	O(1W)^v	Ca	O(2W)^i	80.02(9)
O(1)^i	Ca	O(2W)^v	86.37(7)	O(1W)^v	Ca	O(2W)^v	80.05(8)
O(1)^{iii}	Ca	O(1)^v	74.41(6)	O(2W)^i	Ca	O(2W)^v	102.5(1)
O(1)^{iii}	Ca	O(1)^{vi}	100.57(8)	O(1)^i	S(1)	O(1)^{ii}	102.49(8)
O(1)^{iii}	Ca	O(1W)^i	128.36(7)	O(1)^i	S(1)	O(1)^{iii}	102.49(8)
O(1)^{iii}	Ca	O(1W)^v	76.67(6)	O(1)^{ii}	S(1)	O(1)^{iii}	102.49(8)
O(1)^{iii}	Ca	O(2W)^i	151.54(6)	O(21)^i	S(2)	O(21)^{viii}	105.2(1)
O(1)^{iii}	Ca	O(2W)^v	85.47(7)	O(21)^i	S(2)	O(21)^x	105.2(1)
O(1)^v	Ca	O(1)^{vi}	56.73(7)	O(21)^i	S(2)	O(22)^i	113.4(1)
O(1)^v	Ca	OO(1W)^i	134.27(6)	O(21)^{viii}	S(2)	O(21)^x	105.2(1)
O(1)^v	Ca	O(1W)^v	74.13(7)	O(21)^{viii}	S(2)	O(22)^i	113.4(1)
O(1)^v	Ca	O(2W)^i	86.37(7)	O(21)^x	S(2)	O(22)^i	113.4(1)
O(1)^v	Ca	O(2W)^v	149.78(7)	H(1)	O(1W)	H(2)	108(5)
O(1)^{vi}	Ca	O(1W)^i	78.67(6)	H(3)	O(2W)	H(4)	108(4)

^{a}For symmetry codes see Table 2.

Table 4. Hydrogen bonds in $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$.

Donor–H	Donor···Acceptor	H···Acceptor	Donor–H···Acceptor
O1W–H2 0.729(0.045)	O1W···O21 (0) 2.739(0.004)	H2···O21 (0) 2.106(0.038)	O1W–H2···O21 (0) 145.46(3.39)
O1W–H1 0.746(0.033)	O1W···O1W (1) 3.107(0.003)	H1···O1W (1) 2.723(0.041)	O1W–H1···O1W (1) 114.45(3.13)
O1W–H1 0.746(0.033)	O1W···O2W (2) 3.111(0.004)	H1···O2W (2) 2.424(0.035)	O1W–H1···O2W (2) 153.71(4.18)
O1W–H2 0.729(0.045)	O1W···O21 (3) 3.350(0.004)	H2···O21 (3) 2.786(0.034)	O1W–H2···O21 (3) 136.03(4.16)
O2W–H3 0.731(0.053)	O2W···O21 (3) 2.780(0.005)	H3···O21 (3) 2.111(0.057)	O2W–H3···O21 (3) 152.61(4.26)
O1W–H2 0.729(0.045)	O1W···O22 (4) 2.956(0.003)	H2···O22 (4) 2.237(0.044)	O1W–H2···O22 (4) 168.39(3.61)
O1W–H2 0.729(0.045)	O1W···O22 (5) 2.955(0.003)	H2···O22 (5) 2.236(0.044)	O1W–H2···O22 (5) 168.40(3.61)
O1W–H2 0.729(0.045)	O1W···O22 (6) 2.955(0.003)	H2···O22 (6) 2.237(0.044)	O1W–H2···O22 (6) 168.37(3.61)
O2W–H3 0.731(0.053)	O2W···O21 (6) 2.746(0.004)	H3···O21 (6) 2.067(0.045)	O2W–H3···O21 (6) 154.99(4.42)
O2W–H4 0.858(0.031)	O2W···O1 (7) 2.755(0.003)	H4···O1 (7) 1.917(0.031)	O2W–H4···O1 (7) 165.22(3.47)

Equivalent positions:

(0) x, y, z
(1) $+x-y, -y, -z+\frac{1}{2}$
(2) $+x-\frac{1}{3}, +x-y+\frac{1}{3}, +z-\frac{1}{6}$
(3) $-y, +x-y+1, +z$
(4) $-x-\frac{2}{3}, -y+\frac{2}{3}, -z+\frac{2}{3}$
(5) $+y-\frac{2}{3}, -x+y-\frac{1}{3}, -z+\frac{2}{3}$
(6) $+x+\frac{1}{3}, +x+\frac{2}{3}m -z+\frac{2}{3}$
(7) $+x+\frac{1}{3}, +x-y+\frac{2}{3}, +z+\frac{1}{6}$

Neutral atom scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_{calc}: the values for f' and f'' were also those of Cromer and Waber.[19] All calculations were performed using the TEXSAN[20] crystallographic software package. Tables 1–4 describe positional parameters, $B(eq)$, intramolecular distances and bond angles and hydrogen bonds for $Ca_3(SO_4)$-$(SO_3)_2 \cdot 12H_2O$. Supplementary material, including tables showing F_o, F_c and U_{ij}, can be obtained from one of the authors (R.M.) upon request.

Discussion

Many sulfites and sulfite hydrates of divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) have been reported in the literature.[13,21–28] All of these compounds are ionic, the cation coordinating to water oxygens and sulfite oxygens. In Table 5 cation sizes[29] and the maximum known number of molecules of water of hydration are listed. It may be noted that $CaSO_3 \cdot 0.5H_2O$ fits excellently into the set, while the tetrahydrate claimed by Shiino *et al.*[12] seems to contain too many waters of hydration.

Our misgivings as to the existence of $CaSO_3 \cdot 4H_2O$ were reinforced by our failure to prepare the compound. Precipitating calcium sulfite from aqueous solution by different techniques invariably produced the hemihydrate, $CaSO_3 \cdot 0.5H_2O$. However, if part of the sulfite is oxidized, as described in the experimental section, $Ca_3(SO_4)(SO_3)_2$-$\cdot 12H_2O$ may be formed.

The tetrahydrate was reported by Matsuno and Koishi[10] and by McCall and Tadros.[11] Shiino *et al.*[12] determined the

Table 5. Cation sizes (calculated for six-coordination)[29] and maximum known number of water molecules of hydration for sulfites of divalent cations.[13,21–28]

Cation	Effective ionic radius/Å	Maximum known number of water molecules of hydration	Ref.
Ni^{2+}	0.690	6	21
Mg^{2+}	0.720	6	22
Zn^{2+}	0.740	3	23
Co^{2+}	0.745	3	22
Fe^{2+}	0.78	3	24
Mn^{2+}	0.81	3	25
Cd^{2+}	0.95	1.5	26
Ca^{2+}	1.00	0.5 (4)	27, 13
Sr^{2+}	1.18	0	28
Pb^{2+}	1.19	0	28
Ba^{2+}	1.35	0	28

cell as rhombohedral ($R\bar{3}c/R3c$). Matsuno et al.[13] solved the crystal structure in monoclinic space group $C2/c$ which may, however, easily be converted into a rhombohedral cell. In their structure report one of the sulfite anions was found to be disordered, and its configuration was reported to resemble that of SO_4^{2-}. Matsuno et al. reported the calculated density of $CaSO_3 \cdot 4H_2O$ to be 1.866 g cm^{-3}, while the measured density determined by flotation was 1.88 g cm^{-3}. The measured density would be expected to be lower than the calculated value. However, if the formula is altered to $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$ the calculated density increases to 1.918 g cm^{-3}.

$Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$ was first reported by Cohen and Zangen.[15] In an attempt to synthesize the tetrahydrate they produced instead the double salt. They claim the compound to be isostructural with the monoclinic ($C2/c$) $CaSO_3 \cdot 4H_2O$ described by Matsuno et al.[13] Again their powder diffractogram may be indexed in a rhombohedral cell. They apply the results of Matsuno et al. to model an X-ray diffractogram for $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$. They also claim to have found evidence for a range of solid solubility in the system. In a later paper Zangen and Cohen[30] describe the hydrogen-bonding system for $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$. Again they employed the model of Matsuno et al.

We carried out a number of syntheses at different SO_3^{2-}/SO_4^{2-} ratios. No evidence for solid solubility was found, however. The introduction of more than one sulfate per formula unit would force the disorder of the sulfate group to be lifted, otherwise dramatic changes in the cell dimensions would be expected.

Fig. 1 depicts the crystal structure of $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$. Fig. 2 depicts the $[Ca_3(SO_3)_2 \cdot 12H_2O]^{2+}$ complex ion. The structure consists of $(Ca_3(SO_3)_2 \cdot 12H_2O)^{2+}$ units and disordered SO_4^{2-} groups. The trimeric unit is located on a three-fold axis. Calcium is antiprismatically coordinated to eight oxygens, four of them belonging to the two sulfite groups located on the three-fold axis above and
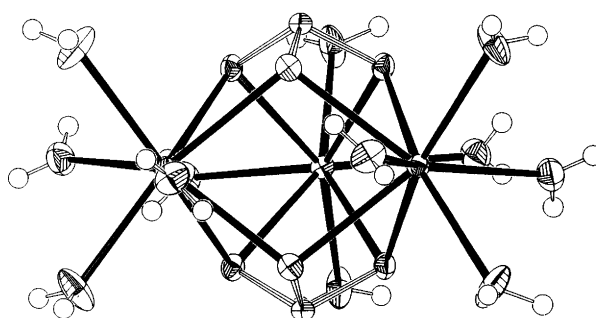

Fig. 2. The $[Ca_3(SO_3)_2 \cdot 12H_2O]^{2+}$ complex ion.

below the Ca plane. The other four, belonging to water molecules, are located at a longer distance from the three-fold axis. The three antiprisms share edges parallel to the three-fold axis. The sulfite groups are bridging as well as chelating, each sulfite oxygen being coordinated to two Ca, and each Ca being coordinated to the two sulfite groups.

The Ca–O polyhedron is similar to those found in Ca-$KAsO_4 \cdot 8H_2O^{31}$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$.[32] The sulfite group's geometry is typical for sulfites of divalent cations, e.g. in $FeSO_3 \cdot 3H_2O$ the distances are 1.530(1), 1.534(1) and 1.545(1) Å, with O–S–O angles of 102.9(1), 104.1(1) and 104.5(1)°.[25]

The sulfate group is disordered on the inverse three-fold axis, the two orientations being flipped over the central sulfur atoms. The structural units are packed in the crystal, so that water layers parallel to c are created. There is a three-dimensional hygrogen-bond net in the crystal (Table 4).

Concluding remark

$Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$ is rhombohedral. We suspect that the tetrahydrate reported by various workers was in fact
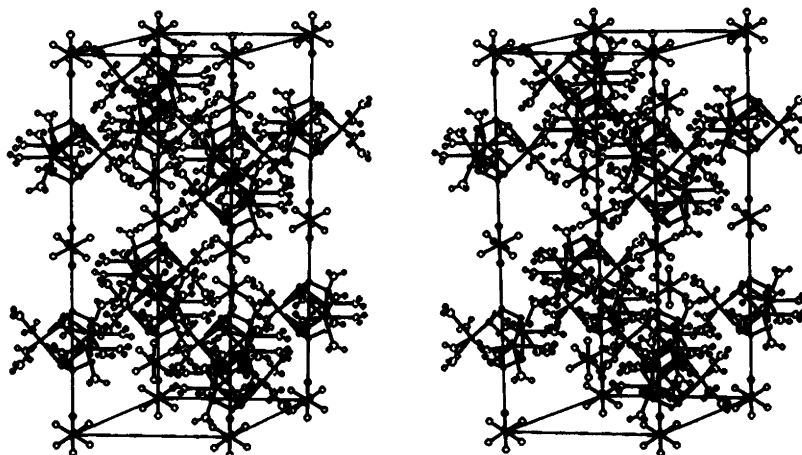

Fig. 1. Stereoscopic packing diagram of $Ca_3(SO_4)(SO_3)_2 \cdot 12H_2O$.

the double salt. However, if a tetrahydrate exists it will not be easily distinguished from the double salt by X-ray powder techniques. No solid solubility was found in the system.

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