

with pentagon-rectangle strips leading to an interconnected infinite network; the same bands can be found in the approximant structure of  $\text{Al}_{13}\text{Co}_4$  connected to periodic nets. Quasiperiodicity, however, is a necessary prerequisite for the existence of an infinite network of interconnected closed icosagonal rings.

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## Structure of Disodium Monocalcium Tartrate Monosuccinate Trihydrate, $\text{Na}_2(\text{CaTMS})\cdot 3\text{H}_2\text{O}$

BY THOMAS J. EMGE,\* JOEL D. OLIVER, DANIEL S. CONNOR AND SUSAN M. THOMAN

*The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239-8707, USA*

AND MARK E. JASON

*The Monsanto Chemical Company, St Louis, Missouri 63167, USA*

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### Abstract

Crystals of disodium monocalcium tartrate monosuccinate (TMS) trihydrate,  $\text{Na}_2\text{Ca}(\text{C}_8\text{H}_6\text{O}_{10})\cdot 3\text{H}_2\text{O}$ ,  $M_r = 402.2$ , are monoclinic, space group  $P2_1/n$  with  $a = 7.989(1)$ ,  $b = 16.543(2)$ ,  $c = 11.416(1)$  Å,  $\beta = 106.48(1)^\circ$ ,  $V = 1446.8(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.846$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.55$  mm<sup>-1</sup> and  $F(000) = 824$ . X-ray intensity data for 3337 independent reflections

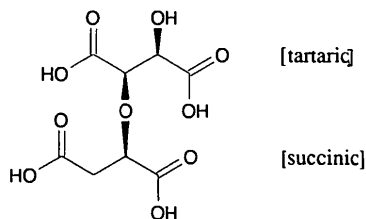
with  $F > 4\sigma(F)$  and  $2\theta < 60^\circ$  were measured. The structure was refined to  $R(F) = 0.031$ . The crystalline phase studied here is the sodium salt of a  $\text{Ca}(\text{TMS})^{2-}$  complex, with edge-bridged trigonal bipyramidal and octahedral geometries for the  $\text{Na}^+$  ions and a dodecahedral geometry for the eight-coordinate  $\text{Ca}^{2+}$  ion. The O atoms from the ether moiety and three carboxylate groups of the TMS anion participate in a tetradentate binding to the  $\text{Ca}^{2+}$  ion. The  $\alpha$ -hydroxycarboxylate group of the tartrato portion of the anion exhibits bidentate binding to the  $\text{Ca}^{2+}$  ion and one carboxylate group serves as a bidentate chelate

\* Current affiliation: Chemistry Department, Wright-Rieman Laboratories, Rutgers University, Piscataway, NJ 08855-0939, USA.

to an Na<sup>+</sup> ion. All three water molecules are ordered and link portions of the anion to nearby cations *via* hydrogen bonding.

### Introduction

Multicarboxylate anions, such as citrate (Okumura, Umehara & Yoneyama, 1987), carboxymethyloxysuccinate (Viccaro & Ambye, 1973), carboxymethyltartrate (Gledhill, 1978) and polyglyoxylate (Park, Jenkins, Holsen, Warnock & Gledhill, 1989), have been investigated for use as builders in detergents and cleaners. For consumer product applications, these compounds are often preferred over phosphates and other chelating agents, *e.g.* nitrilotriacetic acid (NTA) (Pollard, 1966), because of health or environmental concerns (Gledhill, 1978; Park *et al.*, 1989; Epstein, 1972). A highly efficient, metal-chelating multicarboxylate anion, ethylenediaminetetraacetic acid (EDTA), has been used widely for quantitative chemical analyses of metals (Gardiner, 1976). In studies of the sequestering abilities of EDTA and other multicarboxylate anions, stability constant data for their metal complexes have been reported (Martell & Smith, 1982; Smith & Martell, 1987; Smith, Martell & Motekaitis, 1985; Motekaitis & Martell, 1984). Like EDTA, the tartrate monosuccinate (TMS) anion of the title compound is a tetracarboxylate ion with a high binding potential for calcium or transition-metal ions (Motekaitis & Martell, 1989). The crystal structure analysis reported here was undertaken to determine the conformation of the TMS anion (illustrated below in its protonated form and indicating the tartaric and succinic acid residues) and confirm the polydentate nature of TMS as a Ca<sup>2+</sup>-binding ligand.



### Experimental

Na<sub>2</sub>Ca(C<sub>8</sub>H<sub>6</sub>O<sub>10</sub>).3H<sub>2</sub>O was prepared from the mixed sodium salts of DL-tartrate monosuccinate and DL-tartrate disuccinate as described by Bush, Connor, Heinzman & Mackey (1987). The tetrasodium salt of racemic (*RRR/SSS*)-tartrate monosuccinate was precipitated from a highly concentrated (50 wt% water) aqueous solution of the above product mixture by the addition of a small amount of methanol (5 wt%). The solid which resulted was rinsed with 50% aqueous methanol, then dried. The tetrasodium salt, 83.85 g (0.237 mol), was dissolved in 500 ml water and 25.11 g of 88% formic acid (0.48 mol).

Table 1. Atomic coordinates ( $\times 10^5$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^4$ ) for Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. Estimated standard deviations are in parentheses.

	$x$	$y$	$z$	$U_{eq}$
Ca(1)	82961 (4)	41321 (2)	50335 (3)	164 (1)
Na(1)	17091 (10)	66058 (4)	6615 (6)	268 (2)
Na(2)	116366 (10)	24683 (5)	14123 (7)	334 (2)
O(1)	59082 (14)	45391 (6)	32617 (9)	165 (3)
O(2)	30996 (21)	46889 (8)	43591 (12)	394 (5)
O(3)	23383 (18)	59517 (7)	29325 (11)	278 (4)
O(4)	21941 (19)	52474 (7)	12345 (11)	319 (4)
O(5)	34083 (16)	27814 (7)	33387 (11)	263 (4)
O(6)	58794 (16)	32478 (7)	45972 (11)	276 (4)
O(7)	79416 (17)	61512 (7)	22963 (11)	279 (4)
O(8)	88937 (16)	53491 (7)	39169 (10)	256 (4)
O(9)	89964 (17)	35932 (8)	33119 (11)	295 (4)
O(10)	89704 (19)	31694 (9)	14686 (12)	363 (5)
O(1W)	103933 (19)	71361 (8)	39931 (13)	297 (4)
O(2W)	47645 (20)	69995 (9)	10559 (15)	377 (5)
O(3W)	85101 (21)	62998 (9)	- 810 (13)	347 (5)
C(1)	43546 (19)	40604 (8)	28906 (13)	151 (4)
C(2)	45898 (20)	32923 (9)	36712 (13)	167 (4)
C(3)	28079 (22)	45203 (10)	30921 (15)	216 (5)
C(4)	24229 (21)	53094 (9)	23617 (15)	201 (5)
C(5)	64720 (20)	48986 (9)	22886 (13)	169 (4)
C(6)	78801 (20)	55204 (9)	28833 (14)	184 (4)
C(7)	71300 (23)	42754 (10)	15253 (14)	225 (5)
C(8)	84639 (21)	36322 (10)	21618 (15)	217 (5)

The clear solution was heated to 331 K, followed by the slow addition of 21.82 g (0.218 mol) of calcium carbonate. The solution was heated to 353 K, held for 15 min and filtered hot. The pH of the filtrate was raised to 6.1 with 50% aqueous sodium hydroxide. The solution was allowed to evaporate very slowly for 24 d, at which point well formed crystals had grown.

A clear hexagonal rod-shaped crystal, 0.16  $\times$  0.18  $\times$  0.37 mm, was mounted on a Siemens R3m/E diffractometer at room temperature. Graphite-monochromatized Mo  $K\alpha$  ( $\lambda = 0.71069$  \AA) X-radiation was used. Unit-cell dimensions were obtained from 25 reflections with  $33 < 2\theta < 40^\circ$ . Observed systematic absences,  $h0l$ ,  $h + 1 = \text{odd}$ , and  $0k0$ ,  $k = \text{odd}$ , were consistent with space group  $P2_1/n$ . An  $\omega$ -scan method was used for intensity data collection, with a scan range of  $1.4^\circ$ , variable scan speeds of  $4\text{--}30^\circ \text{min}^{-1}$  and a scan:background counting time ratio of 1.0. The 8956 reflections collected in the range  $4 < 2\theta < 60^\circ$  yielded 4214 unique data ( $R_{int} = 0.022$ ). The 3337 unique data with  $F > 4\sigma(F)$  were used in the structural refinement. Data collection limits on indices were:  $0 < h < 11$ ,  $-23 < k < 23$  and  $-16 < l < 15$ . The three intensity standards, which were checked after every 97 data items, showed no significant variation in intensity during the course of the data collection. Intensity corrections for the Lorentz and polarization effects were made. A semi-empirical absorption correction was made, which was based on 720  $\psi$ -scan data and gave minimum and maximum transmission factors of 0.87 and 0.90, respectively. The structure was solved by direct methods. The positions and anisotropic thermal parameters for all non-H atoms were refined to convergence by a full-matrix least-

Table 2. Bond lengths (Å) and angles (°) for Na<sub>2</sub>(CaTMS)<sub>3</sub>H<sub>2</sub>O

Estimated standard deviations are in parentheses.

O(1)—C(1)	1.431 (2)	C(1)—C(2)	1.533 (2)
O(1)—C(5)	1.440 (2)	C(1)—C(3)	1.523 (2)
O(2)—C(3)	1.426 (2)	C(3)—C(4)	1.532 (2)
O(3)—C(4)	1.258 (2)	C(5)—C(6)	1.533 (2)
O(4)—C(4)	1.252 (2)	C(5)—C(7)	1.536 (2)
O(5)—C(2)	1.243 (2)	C(7)—C(8)	1.535 (2)
O(6)—C(2)	1.252 (2)	Na(1)—O(3)	2.721 (2)
O(7)—C(6)	1.249 (2)	Na(1)—O(4)	2.342 (1)
O(8)—C(6)	1.259 (2)	Na(1)—O(2W)	2.442 (2)
O(9)—C(8)	1.262 (2)	Na(1)—O(5) <sup>iii</sup>	2.270 (1)
O(10)—C(8)	1.248 (2)	Na(1)—O(10) <sup>v</sup>	2.366 (2)
Ca(1)—O(1)	2.448 (1)	Na(1)—O(3W) <sup>v</sup>	2.505 (2)
Ca(1)—O(6)	2.360 (1)	Na(2)—O(10)	2.442 (2)
Ca(1)—O(8)	2.500 (1)	Na(2)—O(3 <sup>v</sup> )	2.679 (1)
Ca(1)—O(9)	2.365 (1)	Na(2)—O(5) <sup>iii</sup>	2.311 (1)
Ca(1)—O(2) <sup>v</sup>	2.443 (2)	Na(2)—O(6) <sup>iii</sup>	2.313 (1)
Ca(1)—O(3) <sup>v</sup>	2.517 (2)	Na(2)—O(1W) <sup>iv</sup>	2.602 (2)
Ca(1)—O(8) <sup>iii</sup>	2.385 (1)	Na(2)—O(3W) <sup>v</sup>	2.525 (2)
Ca(1)—O(1W) <sup>iv</sup>	2.464 (1)		
O(1)—C(1)—C(2)	109.5 (1)	O(4)—C(4)—C(3)	116.0 (1)
O(1)—C(1)—C(3)	110.6 (1)	O(1)—C(5)—C(6)	106.6 (1)
C(2)—C(1)—C(3)	107.3 (1)	O(1)—C(5)—C(7)	113.1 (1)
O(5)—C(2)—O(6)	126.1 (1)	C(6)—C(5)—C(7)	112.1 (1)
O(5)—C(2)—C(1)	115.4 (1)	O(7)—C(6)—O(8)	125.3 (1)
O(6)—C(2)—C(1)	118.4 (1)	O(7)—C(6)—C(5)	117.3 (1)
O(2)—C(3)—C(1)	110.2 (1)	O(8)—C(6)—C(5)	117.4 (1)
O(2)—C(3)—C(4)	109.6 (1)	C(5)—C(7)—C(8)	120.0 (1)
C(1)—C(3)—C(4)	112.9 (2)	O(9)—C(8)—O(10)	123.7 (2)
O(3)—C(4)—O(4)	126.0 (1)	O(9)—C(8)—C(7)	120.8 (2)
O(3)—C(4)—C(3)	118.0 (1)	O(10)—C(8)—C(7)	115.6 (1)
C(4)—O(3)—Ca(1) <sup>v</sup>	119.1 (1)	C(4)—O(3)—Na(1)	82.2 (1)
C(4)—O(3)—Na(2) <sup>v</sup>	151.4 (1)	Ca(1 <sup>v</sup> )—O(3)—Na(1)	150.4 (1)
Ca(1 <sup>v</sup> )—O(3)—Na(2) <sup>v</sup>	85.4 (1)	Na(1)—O(3)—Na(2) <sup>v</sup>	81.5 (1)
O(1)—Ca(1)—O(6)	66.2 (1)	O(2 <sup>v</sup> )—Ca(1)—O(3 <sup>v</sup> )	63.5 (1)
O(1)—Ca(1)—O(8)	64.8 (1)	O(1)—Ca(1)—O(8 <sup>v</sup> )	135.9 (1)
O(6)—Ca(1)—O(8)	130.9 (1)	O(6)—Ca(1)—O(8 <sup>v</sup> )	157.9 (1)
O(1)—Ca(1)—O(9)	74.3 (1)	O(8)—Ca(1)—O(8 <sup>v</sup> )	71.2 (1)
O(6)—Ca(1)—O(9)	87.9 (1)	O(9)—Ca(1)—O(8 <sup>v</sup> )	98.2 (1)
O(8)—Ca(1)—O(9)	75.8 (1)	O(2 <sup>v</sup> )—Ca(1)—O(8 <sup>v</sup> )	90.6 (1)
O(1)—Ca(1)—O(2)	72.8 (1)	O(3 <sup>v</sup> )—Ca(1)—O(8 <sup>v</sup> )	87.9 (1)
O(6)—Ca(1)—O(2)	98.2 (1)	O(1)—Ca(1)—O(1W) <sup>iv</sup>	137.6 (1)
O(8)—Ca(1)—O(2)	70.8 (1)	O(6)—Ca(1)—O(1W) <sup>iv</sup>	77.6 (1)
O(9)—Ca(1)—O(2)	140.5 (1)	O(8)—Ca(1)—O(1W) <sup>iv</sup>	142.9 (1)
O(1)—Ca(1)—O(3 <sup>v</sup> )	117.6 (1)	O(9)—Ca(1)—O(1W) <sup>iv</sup>	83.3 (1)
O(6)—Ca(1)—O(3 <sup>v</sup> )	78.1 (1)	O(2 <sup>v</sup> )—Ca(1)—O(1W) <sup>iv</sup>	136.2 (1)
O(8)—Ca(1)—O(3 <sup>v</sup> )	129.2 (1)	O(3 <sup>v</sup> )—Ca(1)—O(1W) <sup>iv</sup>	73.0 (1)
O(9)—Ca(1)—O(3 <sup>v</sup> )	154.5 (1)	O(8 <sup>v</sup> )—Ca(1)—O(1W) <sup>iv</sup>	82.0 (1)
O(3)—Na(1)—O(4)	51.8 (1)	O(10)—Na(2)—O(3 <sup>v</sup> )	129.6 (1)
O(3)—Na(1)—O(2W)	91.5 (1)	O(10)—Na(2)—O(5 <sup>v</sup> )	99.9 (1)
O(4)—Na(1)—O(2W)	97.3 (1)	O(3 <sup>v</sup> )—Na(2)—O(5 <sup>v</sup> )	83.6 (1)
O(3)—Na(1)—O(5 <sup>v</sup> )	83.4 (1)	O(10)—Na(2)—O(6 <sup>v</sup> )	105.0 (1)
O(4)—Na(1)—O(5 <sup>v</sup> )	135.1 (1)	O(3 <sup>v</sup> )—Na(2)—O(6 <sup>v</sup> )	75.6 (1)
O(2W)—Na(1)—O(5 <sup>v</sup> )	82.0 (1)	O(5 <sup>v</sup> )—Na(2)—O(6 <sup>v</sup> )	154.3 (1)
O(3)—Na(1)—O(10 <sup>v</sup> )	165.5 (1)	O(10)—Na(2)—O(1W) <sup>iv</sup>	162.0 (1)
O(4)—Na(1)—O(10 <sup>v</sup> )	114.2 (1)	O(3 <sup>v</sup> )—Na(2)—O(1W) <sup>iv</sup>	68.3 (1)
O(2W)—Na(1)—O(10 <sup>v</sup> )	94.2 (1)	O(5 <sup>v</sup> )—Na(2)—O(1W) <sup>iv</sup>	82.7 (1)
O(5 <sup>v</sup> )—Na(1)—O(10 <sup>v</sup> )	110.6 (1)	O(6 <sup>v</sup> )—Na(2)—O(1W) <sup>iv</sup>	75.7 (1)
O(3)—Na(1)—O(3W) <sup>v</sup>	97.9 (1)	O(10)—Na(2)—O(3W) <sup>v</sup>	75.0 (1)
O(4)—Na(1)—O(3W) <sup>v</sup>	88.4 (1)	O(3 <sup>v</sup> )—Na(2)—O(3W) <sup>v</sup>	151.9 (1)
O(2W)—Na(1)—O(3W) <sup>v</sup>	170.7 (1)	O(5 <sup>v</sup> )—Na(2)—O(3W) <sup>v</sup>	107.6 (1)
O(5 <sup>v</sup> )—Na(1)—O(3W) <sup>v</sup>	99.2 (1)	O(6 <sup>v</sup> )—Na(2)—O(3W) <sup>v</sup>	85.3 (1)
O(10 <sup>v</sup> )—Na(1)—O(3W) <sup>v</sup>	76.7 (1)	O(1W) <sup>iv</sup> —Na(2)—O(3W) <sup>v</sup>	87.3 (1)

Symmetry transformations employed to generate primed atoms: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $2 - x, 1 - y, 1 - z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $1 - x, 1 - y, -z$ ; (v)  $-1 + x, y, z$ ; (vi)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (vii)  $1 + x, y, z$ ; (viii)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ix)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (x)  $2 - x, 1 - y, -z$ .

squares method. The largest shift/e.s.d value in the final cycle of refinement was less than 0.03. The H-atom positions were obtained from an intermediate difference Fourier map and were included in the refinement. The isotropic temperature factors ( $U_{iso}$ ) for alkyl H atoms were fixed to values approximately equal to the equivalent isotropic temperature factor of the corresponding C atom. For the hydroxyl and water H atoms, the  $U_{iso}$

Table 3. Chelate ring geometries for Na<sub>2</sub>(CaTMS)<sub>3</sub>H<sub>2</sub>O

	Ring I*	Ring II	Ring III	Ring IV	Ring V
$D_M$ (Å) <sup>†</sup>	0.01 <sup>‡</sup>	0.1	0.2	0.001	0.002
$T_M$ (°) <sup>†</sup>	125, O(6)	120, O(8)	139, O(9)	119, O(3)	100, O(4)
$D_R$ (Å) <sup>†</sup>	2.628	2.652	2.908	2.612	2.236
$T_R$ (°) <sup>†</sup>	+11.4	+36.0	-49.2 +2.0 <sup>§</sup>	-3.1	-1.5

\* The atoms which defined rings I to V, and were used in the least-squares plane were: I Ca(1), O(1), C(1), C(2), O(6); II Ca(1), O(1), C(5), C(6), O(8); III Ca(1), O(1), C(5), C(7), C(8), O(9); IV Ca(1), O(2), C(3), C(4), O(3); V Na(1), O(3), C(4), O(4).

<sup>†</sup>  $D_M$  is the distance of the metal ion from the least-squares plane;  $T_M$  is the  $M-O(A)-C(A)$  angle;  $D_R$  is the  $O(A)\cdots O(B)$  distance;  $T_R$  is the  $O(A)-C(A)-X-O(B)$  torsion angle illustrated above.

<sup>‡</sup> Estimated standard deviations are  $\pm 0.003$  Å for  $O\cdots O$  distances and  $\pm 0.4^\circ$  for  $O-C-C-O$  torsion angles.

<sup>§</sup> There are two torsion angles for ring III: O(1)—C(5)—C(7)—C(8) and C(5)—C(7)—C(8)—O(9).

Table 4. Hydrogen-bonding geometries for Na<sub>2</sub>(CaTMS)<sub>3</sub>H<sub>2</sub>O

Contact atoms	Water H-atom contact distances and angles*		
	O $\cdots$ O distance (Å)	H $\cdots$ O distance (Å)	O—H $\cdots$ O angle (°)
O(1W) <sup>iv</sup> —H(1WB) <sup>v</sup> ⋯O7	2.844	1.97	161
O(2W) <sup>v</sup> —H(2WB) <sup>v</sup> ⋯O7	2.894	2.03	176
O(3W) <sup>v</sup> —H(3WB) <sup>v</sup> ⋯O7	2.886	2.12	166
O(1W <sup>v</sup> )—H(1WA <sup>v</sup> ) <sup>v</sup> ⋯O(2W) <sup>†</sup>	2.918	2.22	160
O(2W) <sup>v</sup> —H(2WA <sup>v</sup> ) <sup>v</sup> ⋯O(9) <sup>‡</sup>	2.837	2.07	155
O(3W) <sup>v</sup> —H(3WA <sup>v</sup> ) <sup>v</sup> ⋯O(4) <sup>‡</sup>	2.860	2.01	169

\* Estimated standard deviations are  $\pm 0.003$  Å for  $O\cdots O$  distances,  $\pm 0.05$  Å for  $H\cdots O$  distances and  $\pm 4^\circ$  for  $O-H\cdots O$  angles.

<sup>†</sup> Symmetry operation applied to atoms O(1W) and H(1WA) to generate O(1W<sup>v</sup>) and H(1WA<sup>v</sup>) is  $-0.5 + x, 1.5 - y, -0.5 + z$ .

<sup>‡</sup> Symmetry operations applied to atoms O(9) and O(4) to generate atoms O(9<sup>v</sup>) and O(4<sup>v</sup>) are  $1.5 - x, 0.5 + y, 0.5 - z$  and  $1 - x, 1 - y, -z$ , respectively.

values were set equal to two times the  $U_{eq}$  values of the corresponding O atom. Additionally, the coordinates of atom H(2O) of the hydroxyl group were fixed to the position of the largest ( $\sim 0.6 e \text{ \AA}^{-3}$ ) of three difference Fourier peaks located near O(2). The final  $R$  indices were:  $R(F) = 0.031$  and  $wR(F) = 0.036$ , using 261 variable parameters ( $p$ ), 3337 significant unique data ( $n$ ) and weights  $w = 1/[\sigma^2(F_o) + 0.0003(F_o)^2]$ . The goodness of fit was 1.196. Values for  $R(F)$  and  $wR(F)$  for all 4214 unique data were 0.045 and 0.039, respectively. The minimum and maximum residual electron densities of the final difference density map were  $-0.4$  and  $+0.4 e \text{ \AA}^{-3}$ , respectively. All calculations were performed by use of the *SHELXTL-Plus* series of programs (Sheldrick, 1988) on a MicroVAX 3500 computer. The scattering factors and anomalous-dispersion correction factors were taken from Ibers & Hamilton (1974). The refinement results include: Table 1 (non-H-atom coordinates and equivalent isotropic thermal parameters); Table 2 (non-H-atom bond distances and angles); Table 3 (selected

calcium and sodium coordination geometry data); and Table 4 (selected hydrogen-bonding geometries).\*

### Discussion

Fig. 1 shows the molecular structure of the TMS anion and its coordination to the Na<sup>+</sup> and Ca<sup>2+</sup> ions in the crystal structure of Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O. The observed stereochemistry of the TMS racemate in this structure is *RRR/SSS* with respect to the chiral atoms C(1), C(3) and C(5). As demonstrated by the molecular-geometry data in Table 2, the TMS anion contains no unusual bond distances or angles, despite the fact that the TMS anion engages in tetradentate binding to the Ca<sup>2+</sup> ion. Excluding crown ethers, there are less than a dozen instances of tetradentate or higher binding of carboxylate-containing compounds to Ca<sup>2+</sup> found in a local search of the Cambridge Structural Database (CSD) (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979). The ability of the TMS anion to serve as a tetradentate chelating ligand to Ca<sup>2+</sup> ions explains the high stability of the resultant Ca(TMS) complex (Cotton & Wilkinson, 1972).

An interesting feature of the crystal structure of Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O is the coordination of three cations

\* Lists of non-H-atom anisotropic thermal parameters, H-atom coordinates and  $U_{iso}$  values, bond lengths and bond angles including the H atoms, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55891 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0595]

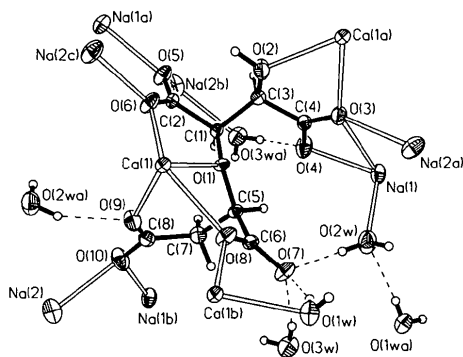


Fig. 1. The molecular structure of Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O. Open bonds indicate calcium and sodium binding and single dashed lines indicate water hydrogen-bonding contacts. Non-H-atom ellipsoids are drawn at the 50% probability level. The H atoms are shown as open spheres of arbitrary diameter. Atoms Na(1a), Na(1b), Na(2a), Na(2b), Na(2c), Ca(1a) and Ca(2b) were generated from atoms Na(1), Na(2) and Ca(1) by symmetry transformations:  $0.5 - x, -0.5 + y, 0.5 - z$ ;  $1 - x, 1 - y, -z$ ;  $1.5 - x, 0.5 + y, 0.5 - z$ ;  $-1 + x, y, z$ ;  $-0.5 + x, 0.5 - y, 0.5 + z$ ;  $1 - x, 1 - y, 1 - z$ ;  $2 - x, 1 - y, 1 - z$ , respectively. Atoms O(1wa), O(2wa) and O(3wa) were generated from atoms O(1), O(2) and O(3) by the symmetry transformations:  $-0.5 + x, 1.5 - y, -0.5 - z$ ;  $1.5 - x, -0.5 + y, 0.5 - z$ ;  $1 - x, 1 - y, -z$ , respectively.

to a single O atom [O(3)] of the  $\alpha$ -hydroxycarboxylate group (see Fig. 1). All the other O atoms in the anion form the expected one or two coordination bonds in which the coordination is within 25° of being along the formal lone-pair vector (assumed coplanar with the carboxylate plane). Atom O(3) is coordinated to Na(1) and Ca(1) using the formal lone pairs, with torsion angles of 179.7(2) and -22.1(2)° for Na(1)—O(3)—C(4)—C(3) and Ca(1)—O(3)—C(4)—C(3), respectively, and to the third cation, Na(2), using an edge-bridging mode with a torsion angle of 123.9(2)° for Na(2)—O(3)—C(4)—C(3). The metal ions are arranged about O(3) with Ca(1a) and Na(2a) positioned -0.816(1) and 1.066(2) Å, respectively, from the least-squares plane defined by the atoms C(3), C(4), O(3) and Na(1). The C—O bond distances about atom C(4) show no unusual effects as a result of the coordination of O(3) to the three cations.

The polyhedra described by the ligand O atoms about each metal ion in Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O are depicted in Fig. 2. The coordination polyhedron of Ca(1) can be described as a slightly distorted dodecahedron. The Na(1) coordination polyhedron consists of an edge-bridged trigonal bipyramid. This geometry is introduced by the asymmetric bidentate binding of Na(1) by one carboxylate group, as indicated by the Na(1)—O(3) [2.721(2) Å] and Na(1)—O(4) [2.342(1) Å] bond distances. The Na(2) coordination polyhedron is a slightly distorted octahedron.

The geometries of the chelate rings in Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O are described in Table 3. The  $D_M$  values reveal that only two of the chelate rings involving the Ca<sup>2+</sup> ion, rings II and III, are significantly non-planar. Table 3 also lists the O...O distances ( $D_R$ ) and O—C—C—O torsion angles ( $T_R$ ) that describe the conformations of the chelate rings. Both rings II and III have half-chair conformations. Examples of both five- and six-membered rings are found in many other Ca carboxylate complexes in the CSD, including calcium malate dihydrate (Branden & Soderberg, 1966), calcium malonate dihydrate (Albertsson, Oskarsson & Svensson, 1978) and calcium  $\alpha$ -ethylmalonate (Zell, Einspahr & Bugg, 1985).

For the Na<sup>+</sup> coordination in Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O, only carboxylate groups and water molecules serve as ligands. The three carboxylate groups coordinated to Na(1) [the

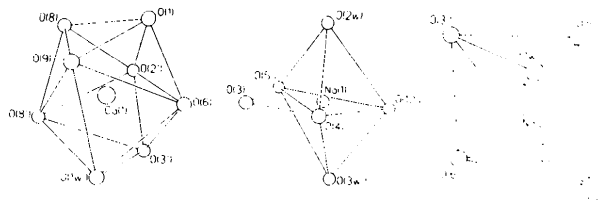


Fig. 2. Representations of the coordination polyhedra for metal ions in Na<sub>2</sub>(CaTMS).3H<sub>2</sub>O: the dodecahedron for Ca(1) (left); the edge-bridged trigonal bipyramid for Na(1) (centre) and the octahedron for Na(2) (right).

carboxylate group containing C(4) serves as a bidentate ligand to Na(1)] and the four carboxylate groups coordinated to Na(2) are from separate TMS anions. The coordination geometries of the calcium and sodium ions in  $\text{Na}_2(\text{CaTMS})\cdot 3\text{H}_2\text{O}$  are illustrated in Fig. 2, which shows that the  $\text{Na}^+$  cations are six-coordinate and the  $\text{Ca}^{2+}$  cation is eight-coordinate. The Ca—O distances range from 2.360(1) to 2.517(2) Å and have an average value of 2.44(6) Å, which is nearly equal to the average Ca—O distance of 2.45 Å for  $\text{Ca}^{2+}$  carboxylate complexes that can be found in the CSD. The Na—O distances have a wider range of values, 2.270(1)–2.505(2) Å for Na(1) [with the  $\mu$ -oxo bridged distance Na(1)—O(3), 2.721(1) Å, omitted] and 2.311(1)–2.679(1) Å for Na(2). The average Na—O distances are 2.38(9) Å for Na(1) and 2.48(15) Å for Na(2) compared to an average value of 2.44 Å obtained from  $\text{Na}^+$  carboxylate complexes that can be found in the CSD.

The individual cation–oxygen bond distances reveal several interesting trends. The three O atoms coordinated to Na(1) in its equatorial plane [O(4), O(5') and O(10')] have the shortest Na—O bond lengths. The bond lengths to the two axial water ligands [O(2W) and O(3W)] have intermediate values. The edge-bridging  $\mu$ -oxo ligand O(3) forms the longest Na—O bond, which is probably the effect of the unusual metal-ion bonding exhibited by this atom. A similar trend in Na—O bond lengths is displayed by Na(2), where the bonds to O(3) and the two water ligands are significantly longer than the remaining three Na—O bonds.

The three molecules of hydration in  $\text{Na}_2(\text{CaTMS})\cdot 3\text{H}_2\text{O}$  are bound to the cations and the TMS anion, with short hydrogen-bonding contacts that involve all six water H atoms (see Fig. 1 and Table 4). On this basis, it is not surprising that all three water molecules exhibit a

high degree of positional order. This situation contrasts that observed in the crystal structures of other Ca multicarboxylate hydrates, such as  $\text{Ca}(\text{CaEDTA})\cdot 7\text{H}_2\text{O}$  (Barnett & Uchtman, 1979) and calcium (–)-hydroxycitrate lactone tetrahydrate (Glusker, Minkin & Casciato, 1971), which contain two or more disordered water molecules.

There are five anion–water and one water–water hydrogen-bonding contacts, all of which have a water molecule donating the H atom, as expected. As shown in Fig. 1, there are three anion–water contacts to O(7), which is the only O atom of the TMS anion that does not bind directly to a cation. There are no significantly short anion–anion contacts in the crystal structure of  $\text{Na}_2(\text{CaTMS})\cdot 3\text{H}_2\text{O}$ . The sodium and calcium ions and the water molecules in this structure serve as the only links between TMS anions. The connectivity of the ions and water molecules is shown by the stereoview of the unit cell in Fig. 3.

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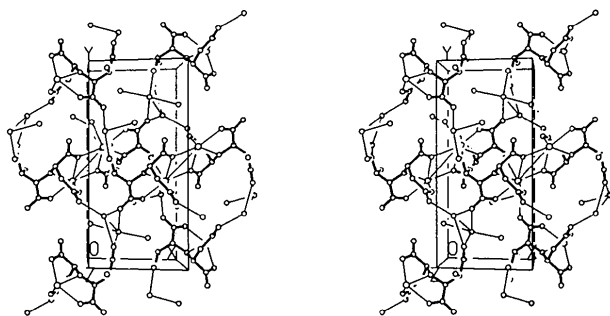


Fig. 3. A stereoview of the unit-cell packing of  $\text{Na}_2(\text{CaTMS})\cdot 3\text{H}_2\text{O}$ , with contacts between anions and water molecules indicated by broken lines. The view is along the crystallographic  $c$  axis, with the  $a$  axis directed from left to right. The H atoms are omitted for clarity.