and the angle between this plane and that of the three Os atoms is 109°.

The Os—Os bond lengths (2·803, 2·838, 2·842 Å) are similar to those found previously; *e.g.* in $[HOs_3(CO)_{10}(CHCH{=}NEt_2)]$ the analogous lengths were 2·785, 2·866 and 2·870 Å (Shapley, Tachikawa, Churchill & Lashewycz, 1978). Os(2) has coordination number 6, while Os(1) and Os(3) have coordination number 7 (including the hydrogen bridge). All three Os atoms obey the effective-atomic-number rule; Os(1)—Os(2), Os(3)—Os(2) have a formal metal–metal bond order of 1. Os(1)—Os(3) is shortened by the two bridging groups, as was found in $[H_2Os_3(CO)_{10}]$ itself where the bond lengths are 2·683, 2·814, 2·815 Å (Broach & Williams, 1979).

The arrangement of the CO groups about Os(2) of the $Os(CO)_4$ group is identical to that in $[HOs_3(CO)_{10}(C_2H_3)]$ (Orpen, Rivera, Bryan, Pippard, Sheldrick & Rouse, 1978) and $[HOs_3(CO)_{10}(p\text{-}CH_3C_6H_4{-}NC(H)O)]$ (Adams & Golembeski, 1979) but differs from that in $[HOs_3(CO)_{10}(CF_3CCHCF_3)]$ (Laing, Sommerville, Dawoodi, Mays & Wheatley, 1978). In this latter compound, Os(2) is σ-bonded to a C atom, thus raising its coordination number to 7 while simultaneously forcing a change in orientation of the $Os(CO)_4$ moiety. The angle C(21)—Os(2)—C(23) in this compound clearly exceeds 90°, as does its geometric analogue in the present case, C(22)—Os(2)—C(23), which is 105°.

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The Structure of Calcium Methanedisulfonate Trihydrate

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Abstract. $[Ca(CH_2O_6S_2)(H_2O)_3]$, $CH_8CaO_9S_2$, monoclinic, $P2_1/n$, $a = 5{\cdot}777\,(1)$, $b = 19{\cdot}469\,(4)$, $c = 7{\cdot}748\,(2)$ Å, $\beta = 92{\cdot}98\,(2)°$, $V = 870{\cdot}3$ Å^3, $Z = 4$, $d_c = 2{\cdot}05$, $d_m = 2{\cdot}03$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·2 mm^{-1}, $R = 0{\cdot}033$ and $R_w = 0{\cdot}051$ for 1451 counter-collected reflections. The sevenfold, approximately pentagonal bipyramidal, coordination polyhedron around the Ca^{2+} ion consists of three water molecules and four sulfonate O atoms from three different methanedisulfonate ions. The methanedisulfonate ligand binds one Ca^{2+} ion forming a six-membered chelate ring and is linked to two other Ca^{2+} ions by unidentate bridging bonds. The ligand occurs in a conformation which has approximate C_{2v} symmetry.

Introduction. Colorless single crystals were readily grown by evaporation from an aqueous solution of the 1:1 salt. From indexed Weissenberg photographs the crystals were found to be monoclinic and the systematic absences $h + l$ odd for $h0l$ and k odd for $0k0$ indicated space group $P2_1/n$ [a non-standard setting for $P2_1/c$ with general positions $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$]. A single crystal with approximate dimensions 0·3 × 0·3 × 0·2 mm was used to collect accurate unit-cell parameters as well as three-dimensional X-ray intensity data on an automated diffractometer. A total of 1578 data out to $2\theta = 50°$ were collected using Mo $K\alpha$ radiation and the θ–2θ scan technique.

The raw intensity data were assigned e.s.d.'s from

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counting statistics and reduced to values of F_o and $\sigma(F_o)$. A total of 1451 reflections had $F_o > \frac{1}{2}\sigma(F_o)$ and these were used in subsequent calculations.

The structure was solved using a combination of direct and heavy-atom methods. H atoms were located from a difference Fourier synthesis phased by all the non-H atoms which had been anisotropically refined. An isotropic temperature factor of 5·0 Å^2 was assigned to each H atom. The entire structure was refined by a full-matrix least-squares procedure, although the H-atom parameters were not varied. A total of 118 parameters including one scale factor was refined yielding a data: parameter ratio of 12·3 : 1. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, was taken to be $[\sigma(F_o)]^{-2}$. The structure refinement converged to a conventional R index, $\sum||F_o|-|F_c||/\sum|F_o|$, of 0·033 and a weighted R_w index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0·051. In the final least-squares cycle no parameter varied by more than 0·01 times its e.s.d. The goodness-of-fit was 1·72. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of F_o, $\sin\theta/\lambda$ or Miller indices indicated no unusual trends. A final difference synthesis was essentially flat. The neutral scattering factors of all atoms were taken from *International Tables for X-ray Crystallography* (1974) and included corrections for the real and imaginary anomalous dispersion of calcium. The programs used in the solution and refinement of this structure have been described (Karipides, 1979). The final positional parameters are given in Table 1.*

Discussion. A view of the CaO_7 coordination polyhedron, mode of ligand–Ca^{2+} binding and atom-numbering scheme are shown in Fig. 1. The Ca^{2+} ion is seven-coordinate and the CaO_7 polyhedron consists of the Ca^{2+} ion surrounded by four methanedisulfonate O atoms O(1), O(2^{i}), O(4^{ii}), O(5) and three water molecules O(7), O(8), and O(9). The nature of the seven-coordinate geometry for the coordination polyhedron can be estimated using the formalism suggested by Muetterties & Guggenberger (1974) and discussed by Drew (1977). Although examination of the seven-atom shape characteristics reveals a small distortion towards a monocapped octahedron, the polyhedron is best described in terms of a pentagonal bipyramid (Fig. 1). The five atoms O(1), O(5), O(8), O(9) and O(2^{i}) which form the pentagonal girdle of the polyhedron are close to coplanarity. The maximum deviation from the least-squares plane through these atoms is 0·34 Å. The average O—Ca—O angle in the pentagonal girdle is 72·7°. The Ca—O(4^{ii}) and Ca—O(7) axial bond vectors form angles of 3 and 5° respectively, with this pentagonal plane.

Each methanedisulfonate ligand binds three Ca^{2+} ions. One Ca^{2+} ion is coordinated to O atoms O(1) and O(5), forming a highly buckled six-membered chelate ring. In addition, O atoms O(2) and O(4) form single

Table 1. *Positional parameters* ($\times 10^5$ *for non*-H *atoms*; $\times 10^3$ *for* H *atoms) and equivalent isotropic temperature factors with e.s.d.'s*

B_{eq}'s for the non-H atoms were calculated from the deposited anisotropic coefficients following the definition given by Hamilton (1959).

	x	y	z	B_{eq} (Å^2)
Ca	5475 (8)	11227 (2)	24607 (6)	1·18 (3)
S(1)	−16677 (10)	22786 (3)	−8732 (7)	1·22 (3)
S(2)	−47371 (10)	10642 (3)	−4417 (7)	1·11 (5)
O(1)	−4363 (31)	21574 (9)	7876 (23)	1·63 (7)
O(2)	−19406 (33)	30148 (9)	−12144 (26)	2·09 (9)
O(3)	−6870 (32)	19109 (10)	−22804 (23)	2·06 (8)
O(4)	−70518 (31)	9315 (9)	1520 (24)	1·77 (7)
O(5)	−29340 (32)	8682 (9)	8345 (25)	1·97 (9)
O(6)	−44201 (31)	7732 (9)	−21313 (23)	1·85 (8)
O(7)	−21452 (36)	13980 (12)	45071 (24)	2·73 (9)
O(8)	75 (35)	−1111 (10)	23218 (24)	2·14 (9)
O(9)	28262 (56)	5770 (13)	47485 (36)	5·49 (15)
C	−45648 (42)	19738 (12)	−6620 (32)	1·31 (9)
H1(C)	−510	220	33	
H2(C)	−540	216	−173	
H1(O7)	−189	152	559	
H2(O7)	−375	145	428	
H1(O8)	−89	−28	153	
H2(O8)	113	−32	235	
H1(O9)	336	73	570	
H2(O9)	390	55	420	

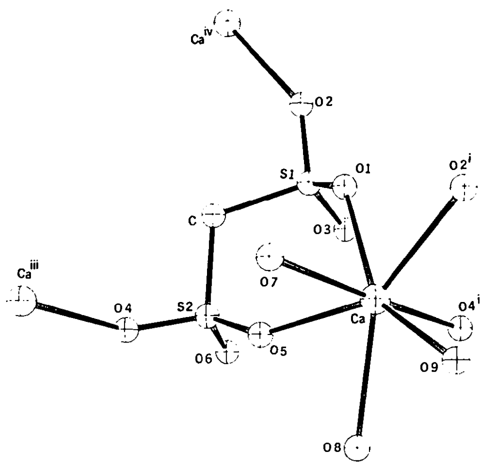

Fig. 1. A view of the structure showing the CaO_7 coordination polyhedron, mode of methanedisulfonate–Ca^{2+} binding and the atom-numbering scheme. H atoms have been omitted for clarity. The superscripts specify the symmetry-related positions of the atoms given in Table 1: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36210 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bridge bonds to two different Ca^{2+} ions which results in a polymeric crystalline structure. Ligand O atoms O(3) and O(6) are not involved in Ca^{2+}-ion binding but they do participate in the hydrogen-bonding scheme.

The 2·349 to 2·446 Å range in Ca–O distances involving sulfonate O atoms is significantly greater than the 2·285 to 2·339 Å spread found in calcium methanesulfonate, $Ca(CH_3SO_3)_2$, where the Ca^{2+} ion is only six-coordinate (Charbonnier, Faure & Loiseleur, 1977). This difference suggests a similar correlation of Ca–sulfonate-oxygen lengths with coordination number in the manner reported for Ca–carboxylate-oxygen distances (Einspahr & Bugg, 1977).

The dimensions of the methanedisulfonate ion given in Table 2 are essentially similar to the values found in potassium methanedisulfonate (Truter, 1962) and silver methanedisulfonate (Charbonnier, Faure & Loiseleur, 1979) which to our knowledge are the only other reported structures containing the methanedisulfonate moiety. The only significant difference is in the S–C–S angle which is considerably more contracted in the Ca salt [113·3 (1)°] than in the K [119·7 (7)°] or Ag [117·7 (7) and 116·4 (7)°] derivatives.

In calcium methanedisulfonate the two sulfonate groups of the ligand are twisted by about 7° from idealized C_{2v} symmetry. In this C_{2v} conformation the O(2)–S(1)–C–S(2)–O(4) grouping forms a planar 'W' (Uchtman & Gloss, 1972; Libson, Deutsch & Barnett, 1980). This same conformation is also found in the K salt and in one of two methanedisulfonate ions present in the Ag compound.

Table 2. *Bond distances* (Å) *and angles* (°)

Superscripts are defined in Fig. 1.

Ca–O(1)	2·446 (2)	S(1)–O(1)	1·457 (2)
Ca–O(2^{i})	2·413 (2)	S(1)–O(2)	1·465 (2)
Ca–O(4^{ii})	2·349 (2)	S(1)–O(3)	1·444 (2)
Ca–O(5)	2·370 (2)	S(2)–O(4)	1·460 (2)
Ca–O(7)	2·340 (2)	S(2)–O(5)	1·450 (2)
Ca–O(8)	2·242 (2)	S(2)–O(6)	1·447 (2)
Ca–O(9)	2·400 (2)	C–S(1)	1·791 (3)
		C–S(2)	1·782 (3)

O(1)–Ca–O(2^{i})	76·73 (6)	O(1)–S(1)–O(2)	111·2 (1)
O(1)–Ca–O(5)	73·92 (6)	O(1)–S(1)–O(3)	113·2 (1)
O(5)–Ca–O(8)	70·45 (6)	O(2)–S(1)–O(3)	113·0 (1)
O(8)–Ca–O(9)	70·03 (8)	O(4)–S(2)–O(5)	112·1 (1)
O(9)–Ca–O(2^{i})	72·50 (7)	O(4)–S(2)–O(6)	112·1 (1)
O(7)–Ca–O(4^{ii})	172·54 (8)	O(5)–S(2)–O(6)	113·2 (1)
O(3)–S(1)–C	108·0 (1)	S(1)–C–S(2)	113·3 (1)
O(2)–S(1)–C	104·4 (1)	O(6)–S(2)–C	107·0 (1)
O(1)–S(1)–C	106·3 (1)	O(5)–S(2)–C	106·6 (1)
		O(4)–S(2)–C	105·2 (1)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor (*D*) and H atoms have the coordinates listed in Tables 1 and 2. The following superscripts specify the symmetry-related positions of the acceptor (*A*) atoms: (v) $x, y, 1+z$; (vi) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $-1-x, -y, -z$; (viii) $-x, -y, -z$; (ix) $1+x, y, 1+z$.

Hydrogen bond	*D*···*A*	H···*A*	*D*–H···*A*
O(7)–H1(O7)···O(3^{v})	2·772 (3)	1·91	165
O(7)–H2(O7)···O(2^{vi})	3·022 (3)	2·14	157
O(8)–H1(O8)···O(4^{vii})	2·966 (3)	2·14	166
O(8)–H2(O8)···O(6^{viii})	2·867 (3)	2·11	170
O(9)–H1(O9)···O(6^{ix})	2·850 (3)	2·06	156

There is an extensive network of hydrogen bonds utilizing five of the six H atoms from the water molecules. All acceptor atoms are sulfonate O atoms. An interesting feature is the non-participation of H2(O9) in the hydrogen-bonding scheme. Although the Ca···H2(O9) distance of 2·56 Å is at the low end of accepted Ca···H contacts involving water molecules, the reported H2(O9) position was clearly indicated in the difference Fourier map (Einspahr & Bugg, 1980). Pertinent hydrogen-bonding parameters are summarized in Table 3.

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