

conséquence directe de la dissymétrie du champ électrique régnant entre deux feuillettes. En effet, dans un feuillette trois sites octaédriques sur quatre sont occupés par du manganèse, le quatrième site étant vacant il y correspond une lacune cationique. L'équilibre des forces électrostatiques impose aux ions  $\text{Cu}^{2+}$  un déplacement en direction de ces lacunes cationiques.

Dans  $\text{Co}_2\text{Mn}_3\text{O}_8$  et  $\text{Zn}_2\text{Mn}_3\text{O}_8$  le degré d'oxydation du manganèse est toujours inférieur à quatre, on peut interpréter ce résultat en admettant une substitution partielle de  $\text{Co}^{2+}$  ou  $\text{Zn}^{2+}$  par  $\text{Mn}^{2+}$ .

Dans  $\text{Cu}_2\text{Mn}_3\text{O}_8$  le degré d'oxydation du manganèse a été trouvé exactement égal à quatre à la précision des mesures près. Cette valeur du degré d'oxydation peut s'expliquer par le polyèdre de coordination très singulier de  $\text{Cu}^{2+}$  qui empêche toute substitution de  $\text{Cu}^{2+}$  par  $\text{Mn}^{2+}$ .

Dans tous les cas le degré d'oxydation du manganèse dans les feuillettes octaédriques  $[\text{Mn}_3\text{O}_8]^{4n-}$  serait toujours exactement égal à quatre, en accord avec les

caractéristiques géométriques des octaèdres: distances métal-oxygène et oxygène-oxygène.

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## The Crystal Structures of Calcium Malonate Dihydrate and Strontium Malonate

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$\text{CaC}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is monoclinic, space group  $C2/m$ , with  $a = 13.8707(4)$ ,  $b = 6.8120(2)$ ,  $c = 6.8040(2)$  Å,  $\beta = 106.289(4)^\circ$ ,  $Z = 4$ . The structure has been refined to  $R = 0.032$ . The malonate ion is coordinated to four different Ca ions forming layers that are stacked along  $a$ . The Ca ion is coordinated by six carboxylate and two water O atoms forming a distorted square antiprism.  $\text{SrC}_2\text{H}_2\text{O}_4$  is orthorhombic, space group  $Pnan$ , with  $a = 6.7538(4)$ ,  $b = 10.6270(8)$ ,  $c = 12.6744(11)$  Å,  $Z = 8$ . The structure has been refined to  $R = 0.026$ . The compound is composed of a three-dimensional network of linked nine-coordinate  $\text{Sr}^{2+}$  complexes. The coordination polyhedron is a distorted tricapped trigonal prism. It contains a six-membered chelate ring, which imposes a conformation on the malonate ion in which the C–C–C angle is  $112.5(3)^\circ$ .

### Introduction

The crystalline state contains substantial information of chemical interest since it represents the atomic arrangement of minimum energy. The energy minimum is a compromise between intra- and intermolecular forces. In order to understand the significance of the geometry of a molecule in the solid state it is necessary to know something about the relative importance of these factors. A study of the same chemical group in several crystalline compounds should provide the necessary information.

The group  $-\text{R}-\text{C}-\text{C}-\text{O}$ , where  $R$  is C, N, O or S,

has been shown to have a preferred planar arrangement in the solid state (Oskarsson, 1973, 1976; Dunitz & Strickler, 1968; Kanters, Kroon, Peerdeman & Schoone, 1967; Leiserowitz & Schmidt, 1965). Because of  $\text{O} \cdots \text{O}$  repulsion this empirical rule cannot be fulfilled in the malonate ion without a severe distortion of the C–C–C angle. Consequently, intermolecular forces are expected to be of great importance in determining the geometry of the malonate ion. So far only

three almost planar malonate ions have been observed in the solid state, namely in KH-mal and  $(-)\text{-}_{589}\text{-}[\text{Co}(\text{NO}_2)_2\text{en}_2](+)\text{-}_{589}\text{-}[\text{Co}(\text{mal})_2\text{en}]$  where the C—C—C angles are in the range 119–125° (Sime, Speakman & Parthasarathy, 1970; Matsumoto & Kuroya, 1972). In the rare-earth malonates the angles between the planes through the carboxylate groups and the C atom chain vary in the range 28–70° (Hansson, 1973a). A systematic study of the malonates with metal ions of Groups I and II should further elucidate the influence of intermolecular forces on the geometry of the malonate ion. This paper reports the crystal structures of Ca malonate dihydrate (Camal) and Sr malonate (Srmal).

### Experimental

Crystals of Camal and Srmal were obtained by dissolving the appropriate hydroxide in an aqueous solution of malonic acid. Slow evaporation at room temperature gave colourless single crystals, which were tabular **c** for Camal and prismatic **c** for Srmal. Weissenberg photographs revealed the Laue class  $2/m$  for Camal. The sys-

tematic absences  $hkl: h + k \neq 2n$  gave  $C2, Cm$  and  $C2/m$  as possible space groups. Srmal is orthorhombic and the systematic absences  $0kl: k + l \neq 2n, h0l: h \neq 2n$  and  $hk0: h + k \neq 2n$  uniquely determine the space group as  $Pnan$ , a different setting of  $Pnna$  (*International Tables for X-ray Crystallography*, 1969).

Table 1 gives information concerning the crystal data, the collection and reduction of the intensity data sets, and the refinements based on them.

The unit-cell dimensions were improved by a least-squares treatment of 45 reflexions (Danielsson, Grenthe & Oskarsson, 1976). A four-circle single-crystal diffractometer (CAD-4) was used for the intensity collection. After every 100 measurements three standard reflexions were checked. No systematic variation in their intensities was observed. The values of  $I$  and  $\sigma_c(I)$  were corrected for Lorentz, polarization and absorption effects [ $\sigma_c(I)$  is based on counting statistics]. The expression  $p = (\cos^2 2\theta + \cos^2 2\theta_M)/(1 + \cos^2 2\theta_M)$  was used in the correction of the polarization effects.  $\theta_M$  is the Bragg angle for the monochromator (8.06° for Mo  $K\alpha$  and 13.28° for Cu  $K\alpha$  radiation).

Table 1. *Crystal data, collection and reduction of the intensity data, and the least-squares refinement*

|  | Camal   | Srmal                              |
|--|---|------------------------------------|
| Composition  | $\text{CaC}_3\text{H}_3\text{O}_4 \cdot \text{H}_2\text{O}$ | $\text{SrC}_3\text{H}_3\text{O}_4$ |
| FW   | 178.1   | 189.6                              |
| Space group  | $C2/m$  | $Pnan$                             |
| $a$ (Å)  | 13.8707 (4)   | 6.7538 (4)                         |
| $b$  | 6.8120 (2)  | 10.6270 (8)                        |
| $c$  | 6.8040 (2)  | 12.6744 (11)                       |
| $\beta$ (°)  | 106.289 (4)   | —                                  |
| $V$ (Å <sup>3</sup> )                                    | 617.1   | 909.7                              |
| $Z$  | 4   | 8                                  |
| $D_x$ (g cm <sup>-3</sup> )                              | 1.92  | 2.78                               |
| Crystal size (mm)  | 0.175 × 0.175 × 0.060                                       | 0.150 × 0.130 × 0.260              |
| Radiation (graphite-monochromated)                       | Mo $K\alpha$  | Cu $K\alpha$                       |
| Take-off angle (°)                                       | 3   | 5                                  |
| $\theta$ interval (°)                                    | 3–30  | 5–70                               |
| $\omega$ - $2\theta$ scan width $\Delta\omega$ (°)       | 0.6 + 1.1 tan $\theta$                                      | 0.6 + 0.4 tan $\theta$             |
| Minimum number of counts in a scan                       | 3000  | 3000                               |
| Maximum recording time (min)                             | 3   | 3                                  |
| $\mu$ (cm <sup>-1</sup> )                                | 9.52  | 173.8                              |
| Range of transmission factor                             | 0.85–0.94   | 0.17–0.65                          |
| Number of measured reflexions                            | 1016  | 844                                |
| Number of reflexions with zero weight ( $I < 0$ )        | 24  | 11                                 |
| Number of reflexions used in the final refinements, $m$  | 992   | 833                                |
| Number of parameters refined                             | 71  | 81                                 |
| $R = \sum   F_o  -  F_c   / \sum  F_o $                  | 0.032   | 0.026                              |
| $R_w = [\sum w( F_o  -  F_c )^2 / \sum w  F_o ^2]^{1/2}$ | 0.037   | 0.031                              |
| $S = [\sum w( F_o  -  F_c )^2 / (m - n)]^{1/2}$          | 1.7   | 2.5                                |
| $C$ (weighting function)                                 | 0.015   | 0.005                              |
| $g \times 10^{-4}$ (extinction)                          | —   | 0.47 (2)                           |
| Mosaic spread (")  | —   | 12.4                               |
| Domain size ( $\times 10^4$ cm)                          | —   | 0.72                               |

## Structure determination and refinement

The position of the Ca ion was deduced from a vector map, which was consistent with the space groups  $C2$  and  $C2/m$ . The centrosymmetric  $C2/m$  was chosen. The remaining non-hydrogen atoms were located from a difference synthesis. Full-matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  with weights  $w^{-1} = \sigma_o^2/4|F_o|^2 + C|F_c|^2$  was performed.  $C$  was adjusted until constant values of  $\langle \sum w(|F_o| - |F_c|)^2 \rangle$  were obtained in different  $|F_o|$  and  $\sin \theta$  intervals. A subsequent difference synthesis with data having  $\sin \theta/\lambda < 0.5$  revealed all the H atoms. One of these, H(4) belonging to the water O(4), is statistically distributed about the mirror plane. The H atoms were included in the model with isotropic temperature factors. In the final cycle the shifts in the parameters were less than 10% of the estimated standard deviations except for the  $B$  value of H(4) (25%). The presence of extinction was investigated by an isotropic model (Zachariasen, 1967), but no such effect was observed. A few cycles of refinement in the space group  $C2$  did not significantly improve the structural model.

The crystal structure of Srml was deduced from vector and difference maps. The parameters were improved by calculations similar to those for Camal. The scattering factor for Sr was corrected for anomalous dispersion. An isotropic extinction correc-

tion was applied. Final difference syntheses were featureless for both structures. Table 2 gives the positional parameters. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).\*

## Description of the structures

Fig. 1 shows the unit cells of Camal and Srml. If we define the packing coefficient as the sum of the van der Waals volumes of the species in a unit cell divided by

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32361 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Some geometrical features of the coordination polyhedra

For Camal the superscripts (i)–(viii) give the transformation applied to the  $x, y, z$  values given in Table 2: (i)  $x, 1 - y, z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, -z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (vi)  $x, y, -1 + z$ ; (vii)  $1 - x, y, 1 - z$ ; (viii)  $x, -y, z$ . For Srml the transformations are: (i)  $x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (ii)  $-\frac{1}{2} + x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $-1 + x, y, z$ ; (iv)  $-\frac{1}{2} + x, -y, z$ ; (v)  $\frac{1}{2} - x, y, 1 - z$ .

## (a) Selected bond distances (Å)

| Camal                   |           |                        |           |
|-------------------------|-----------|------------------------|-----------|
| Ca—O(1)                 | 2.395 (1) | Ca—O(2 <sup>iv</sup> ) | 2.533 (1) |
| Ca—O(1 <sup>i</sup> )   | 2.395 (1) | Ca—O(2 <sup>v</sup> )  | 2.533 (1) |
| Ca—O(1 <sup>iii</sup> ) | 2.523 (1) | Ca—O(3)                | 2.392 (1) |
| Ca—O(1 <sup>iii</sup> ) | 2.523 (1) | Ca—O(4 <sup>vi</sup> ) | 2.367 (1) |

## Srml

|                         |           |                        |           |
|-------------------------|-----------|------------------------|-----------|
| Sr—O(1 <sup>i</sup> )   | 2.639 (2) | Sr—O(3 <sup>iv</sup> ) | 2.770 (3) |
| Sr—O(1 <sup>ii</sup> )  | 2.522 (2) | Sr—O(4)                | 2.628 (2) |
| Sr—O(2)                 | 2.512 (3) | Sr—O(4 <sup>iv</sup> ) | 2.706 (2) |
| Sr—O(2 <sup>i</sup> )   | 2.796 (2) | Sr—O(4 <sup>v</sup> )  | 2.664 (2) |
| Sr—O(3 <sup>iii</sup> ) | 2.532 (2) |                        |           |

(b) Camal. Deviations (Å) from the least-squares planes through O(1), O(3), O(1<sup>i</sup>), O(4<sup>vi</sup>) and O(1<sup>ii</sup>), O(1<sup>iii</sup>), O(2<sup>v</sup>), O(2<sup>vi</sup>). The angle between the planes is 0.03°.

|                     |        |                      |       |
|---------------------|--------|----------------------|-------|
| O(1)                | −0.488 | O(1 <sup>ii</sup> )  | 0.000 |
| O(3)                | 0.442  | O(1 <sup>iii</sup> ) | 0.000 |
| O(1 <sup>i</sup> )  | −0.488 | O(2 <sup>v</sup> )   | 0.000 |
| O(4 <sup>vi</sup> ) | 0.534  | O(2 <sup>vi</sup> )  | 0.000 |

(c) Srml. Twist angles (°) calculated according to model 1 of Dymock & Palenik (1975) and the angles between the planes through the triangles. Triangle 1 is defined by O(1<sup>i</sup>), O(2), O(4), triangle 2 by O(2<sup>i</sup>), O(4<sup>v</sup>), O(3<sup>iv</sup>) and triangle 3 by O(1<sup>ii</sup>), O(3<sup>iii</sup>), O(4<sup>iv</sup>).

| Triangles | Angles between the planes through the triangles | Twist angles |
|-----------|---|--------------|
| 1–2       | 32  | 59           |
| 1–3       | 17  | 17           |
| 2–3       | 16  | 74           |

Table 2. Atomic coordinates with e.s.d.'s

$B(\text{Å}^2)$ , which denotes the isotropic temperature factor, was not refined in Srml, but given a fixed isotropic value of 3.0 Å<sup>2</sup>.

|       | $x$          | $y$          | $z$          | $B$       |
|-------|--------------|--------------|--------------|-----------|
| Camal |              |              |              |           |
| Ca    | 0.72270 (3)  | 0.5          | 0.12300 (5)  |           |
| O(1)  | 0.67724 (9)  | 0.15993 (15) | 0.09094 (16) |           |
| O(2)  | 0.64780 (9)  | 0.16060 (16) | 0.58262 (16) |           |
| O(3)  | 0.62468 (12) | 0.5          | 0.36151 (22) |           |
| O(4)  | 0.58676 (18) | 0.5          | 0.82100 (34) |           |
| C(1)  | 0.64705 (13) | 0.0          | 0.14155 (25) |           |
| C(2)  | 0.57016 (14) | 0.0          | 0.26350 (28) |           |
| C(3)  | 0.62451 (14) | 0.0          | 0.49223 (28) |           |
| H(1)  | 0.528 (1)    | 0.123 (3)    | 0.225 (3)    | 1.9 (3)   |
| H(2)  | 0.637 (2)    | 0.397 (3)    | 0.444 (3)    | 3.4 (5)   |
| H(3)  | 0.539 (3)    | 0.5          | 0.784 (6)    | 5.2 (1.0) |
| H(4)  | 0.589 (5)    | 0.357 (10)   | 0.705 (9)    | 9.5 (2.0) |
| Srml  |              |              |              |           |
| Sr    | 0.10115 (4)  | 0.08983 (3)  | 0.35025 (2)  |           |
| O(1)  | 0.39955 (33) | 0.46051 (23) | 0.27736 (17) |           |
| O(2)  | 0.20541 (36) | 0.31674 (24) | 0.34836 (17) |           |
| O(3)  | 0.74256 (35) | 0.15313 (24) | 0.37456 (19) |           |
| O(4)  | 0.44681 (36) | 0.11784 (21) | 0.44248 (17) |           |
| C(1)  | 0.36855 (49) | 0.37208 (34) | 0.34175 (22) |           |
| C(2)  | 0.54082 (55) | 0.33310 (31) | 0.41286 (26) |           |
| C(3)  | 0.58050 (46) | 0.19191 (32) | 0.40929 (23) |           |
| H(1)  | 0.502 (7)    | 0.363 (4)    | 0.488 (4)    |           |
| H(2)  | 0.154 (7)    | 0.634 (4)    | 0.391 (4)    |           |

the unit-cell volume, its value is 0.81 in Camal and 0.78 in Srmal. The van der Waals volumes have been calculated by the incremental method (Kitaigorodsky, 1973). The van der Waals radii were taken from Bondi (1964) and the radii of  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  were assumed to be 1.05 and 1.25 Å respectively. The packing in Srmal is thus somewhat less dense than in Camal, in spite of the disordered arrangement of H(4) in Camal. The malonate ion has mirror symmetry in Camal. It is coordinated to four different Ca ions forming layers that are stacked along **a**. There are hydrogen bonds within the layers as well as between them. In Srmal the malonate ions are twisted and form a three-dimensional network of linked O polyhedra around  $\text{Sr}^{2+}$  by coordination to six different metal ions. Tables 3, 4 and 5

give selected interatomic distances and angles in the two structures as well as some geometrical features of the coordination polyhedra.

#### The coordination polyhedra

The Ca ion is coordinated by six carboxylate and two water O atoms, forming a distorted square antiprism. The 'square' faces of the antiprism are almost perfectly staggered (Fig. 2). Table 3 shows that the average Ca—O distance for the face O(1), O(3), O(1<sup>i</sup>), O(4<sup>vi</sup>) is 2.39 Å and for the face O(1<sup>ii</sup>), O(1<sup>iii</sup>), O(2<sup>v</sup>), O(2<sup>iv</sup>) 2.53 Å. Both carboxylate groups participate in four-membered chelate rings and O(1) is further coordinated to a second Ca ion. In this way the coordination polyhedra share corners and form a zigzag-shaped chain running parallel to **b**.

In Srmal the malonate ion forms one six- and two four-membered rings. The  $\text{Sr}^{2+}$  ion is coordinated by nine carboxylate O atoms forming a distorted tricapped trigonal prism (Fig. 3). The triangular faces O(1<sup>ii</sup>), O(3<sup>iii</sup>), O(4<sup>iv</sup>) and O(1<sup>i</sup>), O(4), O(3<sup>iv</sup>) connect the polyhedra parallel to **a**, thus forming a zigzag-shaped chain running in this direction. The edges O(2), O(2<sup>i</sup>) and O(4), O(4<sup>v</sup>) connect the polyhedra along **b** and **c**, thus linking the chains to form a three-dimensional network. Finally, the corner O(4<sup>iv</sup>) is shared in the **c** direction. The  $\text{Sr}^{2+}$ — $\text{Sr}^{2+}$  distance is 3.88 Å within a chain. To adjacent chains it is 4.24 and 4.30 Å through edge-sharing and 4.47 Å through corner-sharing.

#### The malonate ions

Fig. 4 shows the malonate ions in Camal and Srmal. Their conformations are radically different. In Camal both carboxylate groups are perpendicular to the plane through the C atoms, as can be seen from the torsion angles in Table 4(a). Similar conformations are found in a Nd malonate (Hansson, 1973b), where the carboxylate groups are twisted 70° out of the C—C—C plane, and in malonic acid (Goedkoop & MacGillavry, 1957)

Table 4. Selected interatomic distances (Å), bond angles (°) and torsion angles (°) in the malonate ions

|             |                     |                                 |            |
|-------------|---------------------|---------------------------------|------------|
| (a) Camal   |                     |                                 |            |
| C(1)—C(2)   | 1.524 (3)           | C(1)—C(2)—C(3)                  | 109.5 (2)  |
| C(2)—C(3)   | 1.527 (3)           | O(1)—C(1)—C(2)                  | 119.3 (1)  |
| C(1)—O(1)   | 1.250 (1)           | O(1)—C(1)—O(1 <sup>viii</sup> ) | 121.3 (2)  |
| C(3)—O(2)   | 1.252 (1)           | C(2)—C(3)—O(2)                  | 119.1 (1)  |
| C(2)—H(1)   | 1.01 (2)            | O(2)—C(3)—O(2 <sup>viii</sup> ) | 121.8 (2)  |
| O(1)···O(2) | 3.482 (1)           | C(1)—C(2)—H(1)                  | 107 (1)    |
|             |                     | H(1)—C(2)—H(1 <sup>viii</sup> ) | 112 (2)    |
|             | O(1)—C(1)—C(2)—C(3) |                                 | −90.7 (2)  |
|             | O(2)—C(3)—C(2)—C(1) |                                 | 88.7 (2)   |
| (b) Srmal   |                     |                                 |            |
| C(1)—C(2)   | 1.529 (5)           | C(1)—C(2)—C(3)                  | 112.5 (3)  |
| C(2)—C(3)   | 1.525 (5)           | O(1)—C(1)—C(2)                  | 117.2 (3)  |
| C(1)—O(1)   | 1.262 (4)           | O(2)—C(1)—C(2)                  | 120.2 (3)  |
| C(1)—O(2)   | 1.252 (4)           | O(1)—C(1)—O(2)                  | 122.6 (3)  |
| C(3)—O(3)   | 1.250 (4)           | C(2)—C(3)—O(3)                  | 119.3 (3)  |
| C(3)—O(4)   | 1.270 (4)           | C(2)—C(3)—O(4)                  | 118.4 (3)  |
| C(2)—H(1)   | 1.04 (5)            | O(3)—C(3)—O(4)                  | 122.4 (3)  |
| C(2)—H(2)   | 0.89 (5)            | H(1)—C(2)—H(2)                  | 113 (4)    |
| O(1)—O(2)   | 2.205 (3)           |                                 |            |
| O(3)—O(4)   | 2.207 (3)           |                                 |            |
| O(2)—O(4)   | 2.924 (3)           |                                 |            |
|             | O(1)—C(1)—C(2)—C(3) |                                 | −128.3 (3) |
|             | O(2)—C(1)—C(2)—C(3) |                                 | 51.4 (4)   |
|             | O(3)—C(3)—C(2)—C(1) |                                 | 116.6 (3)  |
|             | O(4)—C(3)—C(2)—C(1) |                                 | −63.7 (4)  |

Table 5. The geometry of the water molecules and the hydrogen bonds in Camal (distances in Å and angles in °)

|                               |           |  |           |
|-------------------------------|-----------|--|-----------|
| O(3)—H(2)                     | 0.88 (2)  | O(2)···O(4)                                      | 3.076 (2) |
| ∠H(2)—O(3)—H(2 <sup>i</sup> ) | 105 (3)   | O(2)···H(4)                                      | 1.88 (7)  |
|                               |           | ∠O(4)—H(4)···O(2)                                | 156 (5)   |
| O(4)—H(3)                     | 0.64 (4)  |  |           |
| O(4)—H(4)                     | 1.26 (7)  | O(3)···O(4 <sup>vii</sup> )                      | 2.846 (3) |
| ∠H(3)—O(4)—H(4)               | 87 (4)    | O(3)···H(3 <sup>vii</sup> )                      | 2.21 (4)  |
|                               |           | O(4 <sup>vii</sup> )—H(3 <sup>vii</sup> )···O(3) | 177 (5)   |
| O(2)···O(3)                   | 2.728 (1) |  |           |
| O(2)···H(2)                   | 1.85 (2)  |  |           |
| ∠O(3)—H(2)···O(2)             | 170 (2)   |  |           |

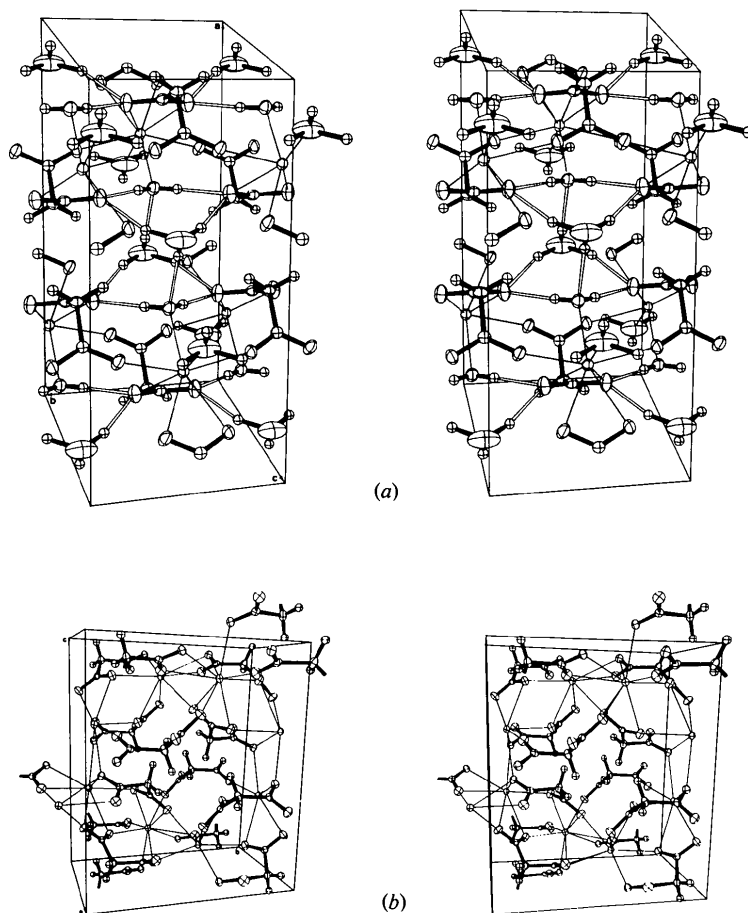


Fig. 1. (a) The structure of Camal. (b) The structure of Srmal.

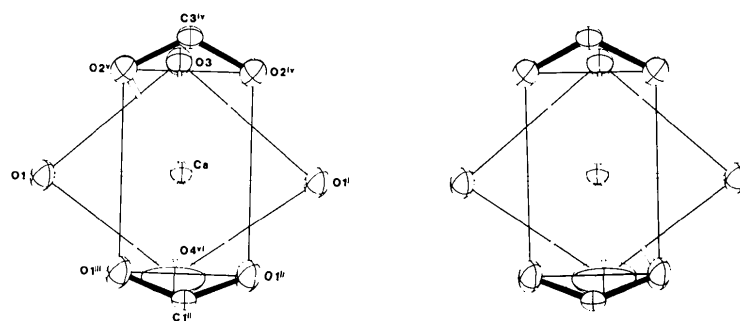


Fig. 2. The coordination polyhedron in Camal.

where one carboxylate group is in the same plane as the C atoms and one is twisted  $90^\circ$  out of this plane. This type of conformation gives a large  $O \cdots O$  separation within the malonate ion (3.48 Å in Camal) so there is no internal strain caused by  $O \cdots O$  repulsion. Conse-

quently the C—C—C angle is close to the tetrahedral value in these compounds.

In Srmal the C—C—C—O torsion angles are  $51.6^\circ$  and  $-63.5^\circ$  (Table 4b), giving a slightly chair-formed chelate ring with  $Sr^{2+}$ . In this conformation the non-

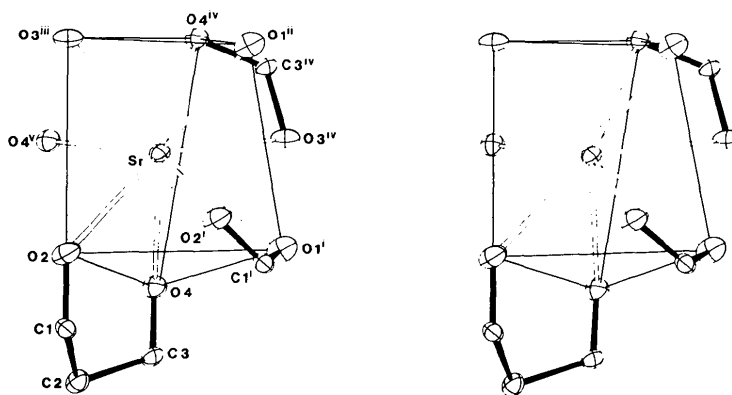


Fig. 3. The coordination polyhedron in Sr mal.

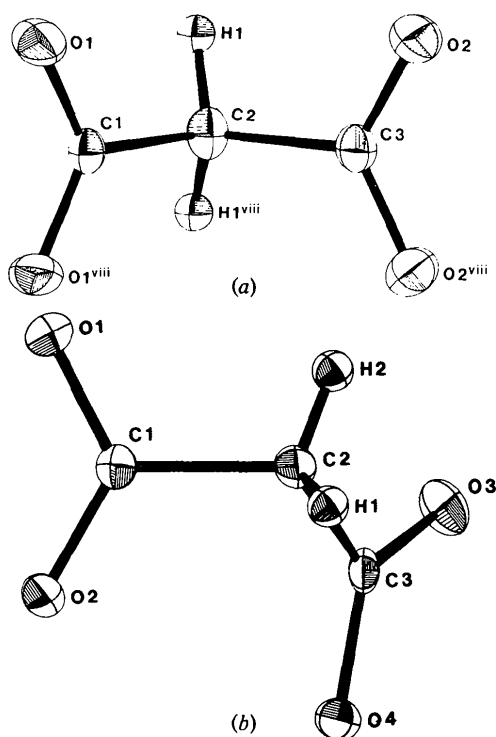


Fig. 4. (a) The malonate ion in Camal. (b) The malonate ion in Sr mal.

bonded  $O(2)\cdots O(4)$  distance is only 2.92 Å. The O—O repulsion causes the  $C(1)-C(2)-C(3)$  angle to be distorted from the tetrahedral value to  $112.5^\circ$ . With a quasi-elastic energy expression,  $U = q\Delta^2/2$ , where  $q$  is the elastic constant and  $\Delta$  the deformation of the angle, the resulting strain energy in Sr mal was calculated as  $150 \text{ J mol}^{-1}$ . Kitaigorodsky's (1973) value of  $30 \text{ kcal mol}^{-1} \text{ rad}^{-2}$  for  $q$  was used. Similar conformations of

the malonate ion are found in rare-earth malonates with six-membered chelate rings (Hansson, 1973a), while in Cd malonate monohydrate (Post & Trotter, 1974) the six-membered chelate ring is so puckered that all the strain energy in the C—C—C angle is relieved.

Related interatomic distances and angles within the four ligand halves  $C-C-O$  are not significantly dif-

ferent (Table 4) and they agree well with those found in other malonate compounds (Hansson, 1973a). If the C—C—C angle is disregarded there are no differences between bond distances and angles in the Camal and Sr mal malonate ions. We thus conclude that primarily only their conformations are affected by intermolecular forces.

#### The water molecules in Camal

The dimensions of the water molecule  $H(2)-O(3)-H(2)$  agree well with those found in other hydrates (Oskarsson, 1974; Ferraris & Franchini-Angela, 1972), while the dimensions of the other water molecule are rather poorly determined (Table 5). This can partly be ascribed to the disordered arrangement of H(4).

In a structural model averaged over the two positions of H(4), the water molecules within the metal-ligand layer participate in an eight-membered hydrogen-bonded ring composed of  $O(3)-H(2)\cdots O(2)\cdots H(4)-O(4)$  and the mirror-related  $H(2')\cdots O(2')\cdots H(4')$ . No individual rings exist, since each 'ring' has only one  $O(4)-H(4)\cdots O(2)$  bond, the mirror-related one being missing. Each quasi-ring is hydrogen-bonded to a centrosymmetrically related one in the next metal-ligand layer through two  $O(4)-H(3)\cdots O(3)$  hydrogen bonds.

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## Changes in Conformation and Bonding of D-Isoascorbic Acid by Ionization. The Crystal Structure of Sodium D-Isoascorbate Monohydrate

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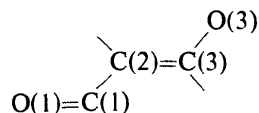
(Received 6 November 1976; accepted 11 December 1976)

Sodium D-isoascorbate monohydrate,  $C_6H_7O_6Na \cdot H_2O$ , is orthorhombic, space group  $P2_12_12_1$ , with  $a = 8.307$  (6),  $b = 9.049$  (2),  $c = 11.181$  (7) Å,  $Z = 4$ . The analysis was performed with 703 counter reflexions, the modified tangent formula and two-dimensional cosine invariants. Refinement was by anisotropic full-matrix least squares to a final  $R$  of 0.042. There are significant differences between the isoascorbate anion and the free acid. In contrast to the acid, the lactone group of the anion is significantly non-planar. As in isoascorbic acid, the side chain adopts a conformation such that O(6) is at the farthest position from the ring. The OH groups and the water molecule participate in hydrogen bonding. The ring and carbonyl O atoms are not involved in hydrogen bonds and O(3), the protolytic O atom, is an acceptor for four hydrogen bonds. The Na ion is surrounded by six O atoms forming a distorted octahedron with  $Na \cdots O$  between 2.296 and 2.386 Å.

### Introduction

D-Isoascorbic acid, also known as D-arabinoascorbic acid, is a stereoisomer of L-ascorbic acid with inversion of the OH group at C(5). The structure of D-isoascorbic acid has been determined by Azarnia, Berman & Rosenstein (1971). The analyses of Na L-ascorbate (Hvoslef, 1969) and L-ascorbic acid (Hvoslef, 1968) have revealed significant bonding and conformational changes in the five-membered rings. The enediol group after dissociation of the H atom at O(3) is no longer planar as in the free acid, whereas the lactone group, which is moderately corrugated in the

acid, remains unaffected. It was also shown that the conjugated system of the ring



undergoes significant change on ionization by lengthening of double bonds and shortening of single bonds.

The authors undertook the present analysis to provide data on the molecular shape for comparison with that of D-isoascorbic acid (Azarnia, Berman & Rosen-