Crystal-Structure Analysis of Weddellite, $CaC_2O_4 . (2+x)H_2O$

By Clarence Sterling

Department of Food Science and Technology, University of California, Davis, California, U.S.A.

Weddellite (calcium oxalate polyhydrate) crystallizes in space group $I4/m$, with the unit-cell dimensions, $a = 12.30$, $c = 7.34$ Å; $Z = 8$. The water content is $2 + x$ ($x \leq 0.5$), the fractional portion being zeolitic. The oxalate ion has at least the symmetry $2mm$ and probably mmm. The calcium ion is coordinated with 8 oxygen atoms, arranged in the form of a distorted cubic antiprism, 8.

Introduction

Weddellite is the tetragonal crystal of a calcium oxalate polyhydrate. It has been found in plants (Frey-Wyssling, 1935; Philipsborn, 1952), in the renal and urinary calculi of animals (Prien & Frondel, 1947; Gasser, Brauner & Preisinger, 1956), in fossil deposits of the Weddell Sea (Bannister & Hey, 1936), and in beer fermentation casks. It has also been produced synthetically (Klasens, Perdok & Terpstra, 1937; Pobeguin, 1943; Honegger, 1952). It has not been the subject of a crystal-structure analysis. Moreover, its exact hydrate composition is moot. The water content in moles per mole of Ca has been given as 3 (Frey-Wyssling, 1935; Klasens, Perdok & Terpstra, 1937; Pobeguin, 1943), as 2·5 (Honegger, 1952), as 2·25 (Walter-Lévy & Laniepce, 1962), as 2 plus a zeolitic quantity up to 2·5 (Philipsborn, 1952), and as 2 (Bannister and Hey, 1936; Gasser, Brauner & Preisinger, 1956).

Materials and methods

Single crystals were supplied from a kidney calculus through the kindness of Prof. A. Preisinger. The powder diagram of this material was that of typical weddellite (Prien & Frondel, 1947; Honegger, 1952). Density was determined by flotation in mixtures of toluene and 1,2-dibromoethane, whose weight was measured in a standard pycnometer. Unit-cell dimensions were obtained with Weissenberg and precession cameras. Intensity data (636 observed and 115 unobserved reflections) were taken photographically *via* the equi-inclination method, the crystal (0.1×0.25 mm) being rotated about [100]. No absorption corrections were applied.

Computations were made on the IBM 7090 and the IBM 7040 computers, with the programs referred to previously (Sterling, 1964).

Results

The unit-cell dimensions are $a = 12.30 \pm 0.02$, $c = 7.34 \pm 0.02$ Å. Density of the fluid in which the crystal just sinks is 2.000 g.cm^{-3}. The closest number of whole molecules of a dihydrate is 8 and of a trihydrate 7. (The calculated density for a dihydrate is 1.962.) For symmetry reasons, the correct number of molecules must be 8, rather than 7. The hydrate state for 8 molecules of salt, with the measured density, corresponds to 2.17.

The only reflections that occur are hkl: $h + k + l = 2n$. The unit cell is thus body-centered, and the systematic extinctions indicate the possible space-groups $I4/m$, $I4$, and $I\bar{4}$. The first of these was favored by Honegger (1952), and subsequently that was found here to be the only one in which the structure could be refined. Because the multiplicity of the general position in $I4/m$ is 16, the calcium atom must occupy a special position and the two or three water oxygen atoms may do so, or may be statistically disordered about special positions.

Positional parameters for Ca, the oxalate group, and one of the water oxygens could be derived from the three-dimensional Patterson distribution. The calcium atom and a water oxygen atom were placed in the mirror plane (001). With a second water oxygen atom also in a position in (001), as reasonably indicated by the Patterson map, the structure of the dihydrate thus obtained was refinable by four least-squares cycles (minimizing $[(w^{\frac{1}{2}}|F_o - F_c|^2)]^{\frac{1}{2}}$, with w assigned unit weight) to yield an R value of 0.179. (R is given by $\Sigma ||F_o| - |F_c||/\Sigma|F_o|$.) A Fourier synthesis of $F_o - F_c$ at this point showed an extra peak, with a maximum density of about 2–3 e.Å^{-3}, on the fourfold axis, relatively remote from the other atoms. This small peak was confirmed in a Fourier synthesis of F_o alone. The peak was taken to represent a third water oxygen atom, whose presence on the fourfold axis would accord with 2·5 molecules of water per calcium atom. However, an oxygen atom in this position, although improving R to 0.174, had a very large thermal parameter ($B = 17$ Å^2).

On the assumption that the crystal is zeolitic, smaller fractions of a water molecule were placed in the indicated position. With 0·4 oxygen atom here, R was lowered to 0.171 and B to 5.7 Å^2. With 0·2 oxygen atom, R was 0.172 and B was negative. Placement of the fractional oxygen atom near, but not on, the four-

Table 1. Observed (FOB) and calculated (FCA) structure factors for weddellite

```
H,L= 0, 0        -5  33  13     5  15  12    -7  42  43    -4 114  98   -14  11  19     3  31 -26    -3 102 106     5  42  47   -14  26  35
K FOB FCA        -7  34  27     7  24  20    -9  35 -38     6   4  -8                    5   4   3    -5  72 -56     7  57 -65
2 151-159        -9  38 -32    -1   4  -6   -11  38  36     8  34  30    H,L= 4, 1        7  23  22    -7  69  64     9  67  83    H,L= 7, 2
4 123 116       -11  26  24    -3   4   8                  10  21  15    K FCB FCA        9  55 -52    -9  28 -22    -1   4  -C    K FLB FCA
6  12 -21       -13  39  35    -5  49 -43    H,L= 2, 6     -2  7C  71     1  16 -11       11  77 -68   -11  21 -19    -3   4  -8     1  19 -14
8  22  20       -15  25 -18                  K FCA FCA    -4  73 -66     3  54 -51       -1  77 -68   -13  36  28    -5  53 -55     3  70 -73
12  47 -47                     H,L= 1, 9     0  66 -68    -8  51 -43     5   4  12       -3  44  39                  -7  40  35     5  22  21
                 H,L= 1, 1     K FOB FCA     2  39  44    -6  31  25     7  21  18       -5   4   8                   -9  53 -62     7  50 -49
H,L= 0, 1        K FOB FCA     0  10   7     4  21 -16   -10   4  -2     9  60 -60       -7  36 -36    H,L= 5, 5     -11  66  73     9   4   6
K FOB FCA        0  17 -21     2  23  24     6  33 -32   -12  13  15    11  58  72       -9  44  38    K FOB FCA    -13  31 -45    11   4   8
0  17 -21        1  16 -21     4  78 -67     8  34  35   -14  29 -29    -1 204-226                     C   4   3                  13  33 -37
1  16 -21        3  22 -26    -2  35 -31    -2  39  44                  -3  81  69    H,L= 4, 8         2  27  24    H,L= 6, 4    -1  37  38
3  22 -26        5  23  24     6 114 129    -4  15  -9    H,L= 3, 4     -5  29  23    K FOB FCA         4  31  28    K FOB FCA    -3  73 -66
5  23  24        7   6   7     8  51 -41    -6  29 -27    K FOB FCA     -7  81 -74     0   4   1        6  35  33    C  55  54    -5  77  84
7   6   7        9  31  33                  -8  24  23     1  32  30    -9  69  64     2  16 -15        8   4 -16    10   4  18    -7  62 -49
9  31  33       11   4   1    H,L= 2, 0    -10  23 -26     3  4C -34   -11  35 -35     4  15  19                    -2   4   4    -9  38  33
11   4   1       13  14  15    K FOB FCA    -12  42 -37     5 108 106   -13  28  35     6   9 -11    H,L= 5, 6     -4  24 -20    -11  17  19
13  14  15       15   9 -11     2  42 -37     4   4   1     7  45 -45                  -2  37 -29    K FOB FCA     -6  28 -27    -13  29 -24
15   9 -11                      4   4   1     6  76 -78     9  21  29    H,L= 4, 2     -4  26  19     1   4   9     8  10 -2C
                 H,L= 0, 2      6  76 -78     8  94  99    -1  28 -19    K FCB FCA     -6  29  19     3  28  29    -8  19  19    H,L= 7, 3
H,L= 0, 2        K FOB FCA      8  94  99    10   4 -28    -3  55 -34    C  35 -47                     5  52 -54    -4  13 -13    K FCB FCA
K FOB FCA        0 104 103     10   4 -28    12  53  48    -5  9C  74     2  37 -36    H,L= 5, 0                   -6   4  -6     0  49  56
0 104 103        2  39 -40     12  53  48                 -7  91 -60     4  26  25    K FCB FCA     H,L= 5, 6     -8  19 -14     2  15  -3
2  39 -40        4  43 -47                  H,L= 1, 2     -9   4  -7     6  35 -33     1  28  19    K FOB FCA    -10  12   8     4  26 -19
4  43 -47        6  46  48    H,L= 1, 2     K FOB FCA    -11  4C  33     8  33 -42     3  9C  93     1   4   9   -12  26 -3C     6  38  35
6  46  48        8  62 -69    K FOB FCA      1  29 -28   -13  27 -23    1C  20  41     5  73 -70     3  28  29                  -2  15  -7
8  62 -69       10  98 101     1  29 -28     3  28 -70                  12   4  -7     7  29  22     5  52 -54    H,L= 6, 5    -4  23  21
10  98 101      12  41 -58     3  28 -70     5  40  29    H,L= 3, 5                    9   4   2                  K FCB FCA    -6  65 -65
12  41 -58      14  11  16     5  40  29     7  46  38   -2 102 -91    H,L= 4, 2     -7  84  79    H,L= 5, 7     1  97-100    -8  42  50
14  11  16      16  14  18     7  46  38    -1  34 -28   -4  36  25    K FOB FCA    -9  39 -38    K FOB FCA     3  52  5C   -10   5  -4
16  14  18                    -1  34 -28    -3   4  -2   -6  42 -36     C   4   5                   C   4   2     5  28 -27   -12  38 -42
                 H,L= 0, 3    -3   4  -2    -5 117 -96   -8  27 -21     2  23 -23    H,L= 5, 7     2   4  12     7   4  -4
H,L= 0, 3        K FOB FCA    -5 117 -96    -7  24 -14  -10  14  14     4  28  22    K FOB FCA     4   4   8     9  32  35    H,L= 7, 4
K FOB FCA        1 110 106    -7  24 -14    -9  25 -21  -12   4   4     6  74 -80     C   4   2     6   4  -8    11  25 -34    K FCB FCA
1 110 106        3  14  15    -9  25 -21   -11  15 -18                  8  25  27     2  15 -7                  -1  94 106     1  17  14
3  14  15        5   4  -4   -11  15 -18                 H,L= 4, 3    10   4   6                  H,L= 6, 6                    3  55 -60
5   4  -4        7  65  56                  H,L= 1, 3    K FCB FCA    12  19 -19    H,L= 5, 7     K FOB FCA    H,L= 7, 5     5  72  64
7  65  56        9  29 -32    H,L= 1, 3    K FOB FCA     1 120 136    -2   4   2    K FOB FCA     C  28  23    K FCB FCA     7  33 -33
9  29 -32       11  21 -13    K FOB FCA     0 109 106     3  70 -66    -4  24  15     C   4   2     2  31 -27     0  18 -17    -1  17  16
11  21 -13      13  12 -12     0 109 106     2  16  11     5  24  20    -6  56  50     2  15 -7     4  41  38     2  37  43    -3  53 -45
13  12 -12                     2  16  11     4 121-110     7  23  21    -8   4 -12     4   4   8     6  18 -22     4  94 -97    -5  26  31
                 H,L= 0, 4     4 121-110    -2 164-171     9  61 -81   -10  26 -21     6   4  -8     8   4  -4     6  26  24    -7  38 -33
H,L= 0, 4        K FOB FCA    -2 164-171    -4 134 136    11  14  25   -12  48  39    -8  32  21    1C  13  15     8  42 -49    -9  18  19
K FOB FCA        0  84 102    -4 134 136    -6  96 -97    13  21 -25                 -10   4  -5     5  43 -43   -1C  15  21   -11  28  32
0  84 102        2  52 -49    -6  96 -97    -8  97  71                 H,L= 3, 6    -12  23 -20    -1  1C  12    -2  13  -7
2  52 -49        4  27 -27    -8  97  71                 H,L= 3, 6    K FOB FCA    -14   4  -9    -3  27  24                  H,L= 7, 6
4  27 -27        6  64  54                 H,L= 2, 2     1  25  15                   -5  46 -43    H,L= 6, 6    K FCB FCA
6  64  54        8  42 -40    H,L= 2, 2    K FOB FCA     3  33 -29    H,L= 5, 2                    K FOB FCA     1  19  21
8  42 -40       10  69  90    K FOB FCA     0  36 -40     5 112 101    K FCB FCA    H,L= 6, 0     1  48 -57     3  64 -55
10  69  90      12  36 -52     0  36 -40     2  93 100     7  28 -25     1  89 -96    K FCB FCA     3  35  31     5  75  79
12  36 -52      14  11  18     2  93 100     4 100 -91     9  17  13     3 146 159     2  73 -69     5   4   7     7  29 -26
14  11  18                     4 100 -91     6  23 -18    11  15  14     5  62 -63     4  57  54     7  21 -31    -1  19  20
                 H,L= 0, 5     6  23 -18     8  65  65    -1   4   6    -1C  41  48     6  27 -25    -3  3C -29    -3  26 -25
H,L= 0, 5        K FOB FCA     8  65  65    10  64 -75    -3  41 -29   -12  22 -24    -2  65 -78    -5   4  -8
K FOB FCA        1   4   1    10  64 -75    -2 110 100    -5  29  29                  -4  36 -36    -7  21  26    H,L= 7, 7
1   4   1        3   4   5    -2 110 100    -4  36 -36    -7  63 -55    H,L= 5, 2    -6  25 -25                  K FCB FCA
3   4   5        5   4   3    -4  36 -36    -6  16   7    -9   4  -0    K FCE FCA    -8  32  21    H,L= 6, 1     0  10  10
5   4   3        7  21 -17    -6  16   7    -8  72  62   -11  17  15     1  89 -96   -10   4  -5    K FOB FCA     2  20  15
7  21 -17        9   4   2    -8  72  62   -10  66 -59                   3 146 159   -12  23 -20     1  74 -83     4  34 -36
9   4   2       11   4  -1   -10  66 -59   -12  43  44    H,L= 3, 7     5  62 -63   -14   4  -9     C  20  2C     6  24  26
11   4  -1                   -12  43  44                  K FOP FCA     7  78  84                   2   4  -1    -2  20 -15
                 H,L= 0, 6                  H,L= 2, 3     C   4  -0     9  37 -50    H,L= 5, 2     4  28 -19    -4  22  22
H,L= 0, 6        K FOB FCA    H,L= 2, 3    K FOB FCA     2  14 -12    11   4   2    K FCE FCA    -2  10  -8    -6  34 -31
K FOB FCA        0 137 148    K FOB FCA     1 159-171     4  44  39    -1  4C  29     1  89 -96    -4   8 -11
0 137 148        2  67 -68     1 159-171     3  71  71     6  32 -29    -3  66  59     3 146 159
2  67 -68        4  26  16     3  71  71     5  33 -26     8  22  21    -5  72 -63    5  62 -63    H,L= 7, 0    H,L= 7, 8
4  26  16        6  30  23     5  33 -26     7  19  -7    -2  29  22    -7  28  21   -1C  41  48    K FOB FCA    K FCB FCA
6  30  23        8   4 -12     7  19  -7     9  36  24    -4  31 -26    -9   4   6   -12  22 -24     1  25  27     1   4   2
8   4 -12       10  29  40     9  36  24    -1  16  11    -6  36  31   -11  39 -42                   3 1C7 -96     3  34 -35
10  29  40      12  37 -41    -1  16  11    -3  27 -21    -8  26 -23   -13  48  50    H,L= 5, 3     5 1CC 1C5    -1  17  20
12  37 -41                    -3  27 -21    -5  36  34                               K FCB FCA     7  47 -42    -3  40 -38
                 H,L= 0, 7    -5  36  34    -7   4  -3    H,L= 3, 8    H,L= 5, 3     0   4  -4    -1  76  87
H,L= 0, 7        K FOB FCA    -7   4  -3    -9  21 -26    K FOB FCA    K FCB FCA     2  36 -30    -3  11 -11    H,L= 8, 0
K FOB FCA        1  21  14    -9  21 -26   -11  65  67     1   4   8     C   4  -4     4   4   7    -5  3C  22    K FCB FCA
1  21  14        3   4  -0   -11  65  67                   3 31 -28     2  36 -36     6  55 -55     C  32  48     2  91  89
3   4  -0        5   4   2                  H,L= 2, 4     5  28  24     4   4   7     8   7   8    -7  47 -47     4  37 -41
5   4   2        7   4  10    H,L= 2, 4    K FOB FCA     7  35 -38     6  55 -55    10   4   8    -9  46  28    -7  87  99
7   4  10        9   4  -1    K FOB FCA     0  51 -49    -1   4   4     8   7   8                 -11  1C  -8    -9  50 -44
9   4  -1       11   4  -3     0  51 -49     2  91  96    -3  37 -28    10   4   8    H,L= 6, 2   -13  49 -51
11   4  -3                     2  91  96     4  51 -5C    -5  92  75                 K FCB FCA                   H,L= 8, 1
                 H,L= 0, 8     4  51 -5C     6  19 -20    -7  34 -35    H,L= 3, 9     0  32  48    H,L= 7, 0    K FCB FCA
H,L= 0, 8        K FOB FCA     6  19 -20     8  33  40                 K FOB FCA    -2  12   7    K FCB FCA     C   8   7
K FOB FCA        C  42  44     8  33  40    10  52 -61     1   4  -2   -2  25  23     4  36 -36     4  37 -41     2  38  32
C  42  44        2  26 -27    10  52 -61    -2  97  96     3  55 -44                 -6  44  47   -11  1C  -8     4  74 -74
2  26 -27        4   4   1    -2  97  96    -4  30 -28     5  71  59    H,L= 4, 0     8 19 -36   -13  49 -51    -1C   4   8
4   4   1        6  21  20    -4  30 -28    -6   4  -3     7  80 -66    K FOB FCA    1C  24  38                  -3  45  46
6  21  20        8  43 -43    -6   4  -3    -8  25  26     9  20  2C     2  55  46    -2  21 -18    H,L= 7, 0
8  43 -43                     -8  25  26   -10  44 -42   -12  30  30     4   4  -2    -4  3C -33    K FOB FCA    H,L= 8, 2
                 H,L= 0, 9    -10  44 -42   -12  30  30                  6  18 -15    -6  24  20    -4  3C -33    K FCB FCA
H,L= 0, 9        K FCB FCA    -12  30  30    H,L= 2, 5    H,L= 3, 9     8  53 -44    -8   4   8    -6  24  20     C   7  -9
K FCB FCA        1   9   7                  K FOB FCA    -5 161 159    1C   4  -8    H,L= 5, 4     4  42  18
1   9   7                     H,L= 2, 5     1  41 -39    -7  87 -73    12  39 -37     1  33 -25    -8   4   4    0  57 -69
                 H,L= 1, 0    K FOB FCA     3   4   2    -9   4  -7    -2   8   1     3  84  74   -1C   4   8    2  49  62
H,L= 1, C        K FUB FCA     1  41 -39     5   4  -7   -11  36  29    -4   4  -8     5  51 -56   -12  31 -32   -2  56  65
3  79  86        3  79  86     3   4   2     7   4  -7   -13  27  26    -6  6C  54    7  24  31
5 169-149        5 169-149     5   4  -7     9  25  33                 -1C  23  24    9  20 -21    H,L= 6, 3
7  89  87        7  89  87     7   4  -7    11  51 -52    H,L= 3, 3                  11   4 -12    K FCP FCA
9  30 -36        9  30 -36     9  25  33   -1  58  5C    K FOB FCA    H,L= 4, 7    13  42  53    1  78 -97
-3  26 -29      -3  26 -29    11  51 -52   -3  23 -23     0  13  15    K FCB FCA   -1  26 -72    3  26  25
                             -1  58  5C   -5  29  24     2  26 -21     1  49  44
```

fold axis led to higher values of B and R and to unreasonable position shifts of that atom. Because 0·4 oxygen atom gives the best computed results and because it represents a hydrate composition of 2·2, close to the measured value of 2·17, that fraction was used in further refinements.

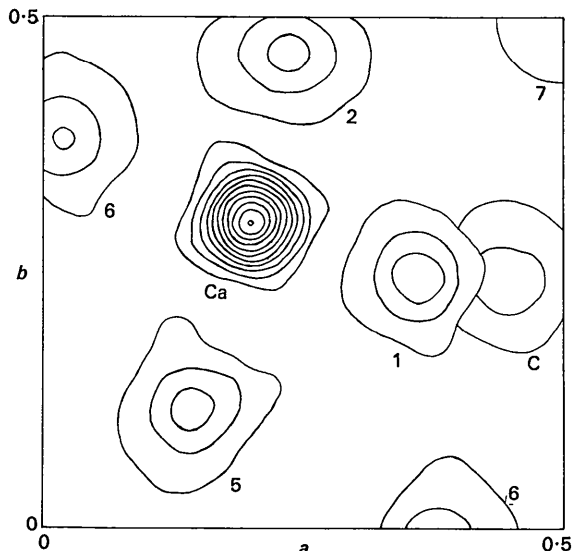Although up to this stage the unobserved reflections were considered as having the F_o value of 0, they were

Fig. 1. Fourier electron-density distribution in asymmetric unit of weddellite. Ca–calcium, C–carbon, numbered atoms–oxygen. Each atom is sectioned in the plane of its maximum electron density.
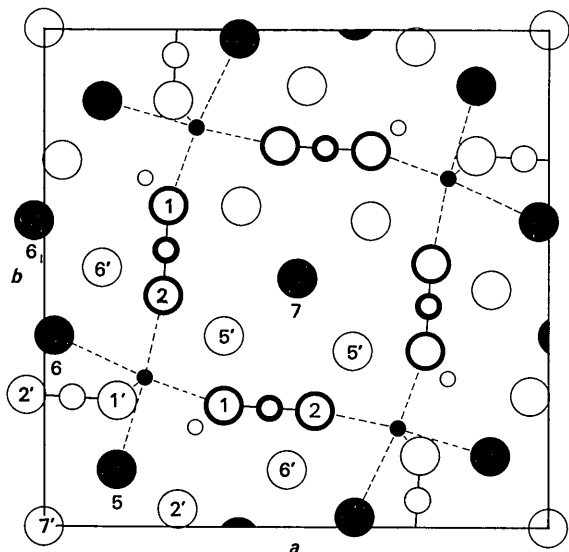
Fig. 2. Cell of weddellite. Atoms of primitive cell have bolder outlines or are solid. Smallest atoms are calcium, next larger ones are carbon, and largest are oxygen, some of which are numbered, as in text and tables (see Table 2, footnote). Atoms of oxalate groups are connected with solid lines. Broken lines connect calcium ions in primitive cell with the oxygen atoms which they are coordinated. Solid oxygen atoms represent water molecules, 5 and 6 lying in the mirror plane (001). The solid calcium atoms also lie in (001).

were next treated as having half the value of the lowest observed intensity. Least-squares refinement on this basis lowered R to 0·141. With the calcium atom permitted anisotropic, instead of isotropic, thermal movement, R could be only slightly improved, to 0·138. (The essentially circular contours of the electron density map of the Ca atom, Fig. 1, also verify an isotropic thermal movement.) Without the unobserved reflections, R is 0·130.

Values of F_o and F_c are presented in Table 1. The Fourier map of the atoms of the asymmetric unit is given in Fig. 1, each atom being sectioned at its peak electron density. The whole cell is shown in Fig. 2, in which it may be seen that the oxalate ions are placed with the C–C bond perpendicular to the (001) plane. Indeed, owing to the symmetry of this space-group, the mirror plane bisects the C–C bond (Fig. 3). Hydrogen atoms could not be detected in a Fourier synthesis of F_o–F_c.

With the numbering of the oxygen atoms as indicated in Figs. 1–3, atomic coordinates and thermal parameters are listed in Table 2. Distances between respective atoms are shown in Table 3 and angles between bonds in Table 4. The calcium atom is coordinated with 8 oxygen atoms (the 2 water oxygen atoms of the dihydrate, 4 oxalate oxygen atoms of its two immediate neighbors in the primitive cell, and 1 oxalate oxygen atom each from the translated primitive cell above and below, respectively). The arrangement of these oxygen atoms is roughly that of a cubic antiprism, 8.

Table 2. *Atomic coordinates and thermal parameters of the asymmetric unit of weddellite*

Atom*	x	y	z	Isotropic temperature factor
Ca	0·200	0·300	0	0·38
O(1)	0·356	0·246	0·181	1·03
O(2)	0·236	0·463	0·181	2·17
O(5)	0·144	0·114	0	1·79
O(6)	0·020	0·386	0	2·50
O(7)	0·500	0·500	0·210	5·61
C	0·445	0·242	0·105	0·91

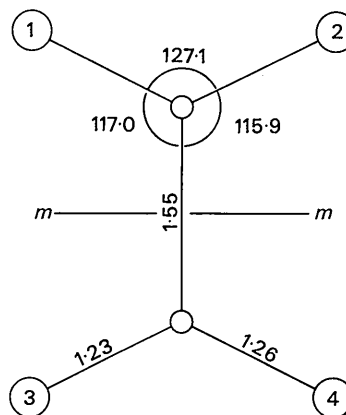* Atom designations for Tables 2–4 are indicated on Figs. 1–3.

Fig. 3. Oxalate ion, as it would be seen in projection on (100). It is bisected by a symmetry plane, *m*.

Table 3. *Interatomic distances in weddellite,*
less than 3·0 Å

Between atoms*	Distance	Standard deviation
Ca–O(5)	2·40 Å	0·01 Å
Ca–O(6)	2·45	0·01
Ca–O(1), O(3)	2·44	0·01
Ca–O(2), O(4)	2·44	0·01
Ca–O(1'), O(3')	2·50	0·01
C(1)–O(1)	1·23	0·01
C(1)–O(2)	1·26	0·01
C(1)–C(2)	1·55	0·02
O(5)–O(1'), O(3')	2·91	0·01
O(5)–O(2'), O(4')	2·93	0·01
O(6)–O(6₁)	2·84	0·02
O(6)–O(2'), O(4')	2·87	0·01

* In Tables 3 and 4, primed numbers refer to a nearby atom of the primitive cell that has been translated to the position $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$. 6_1 is centrosymmetrical to 6 about $0, \frac{1}{2}, 0$.

Table 4. *Bond angles in weddellite*

Atoms*	Angle	Standard deviation
O(1)–C(1)–O(2)	127·1°	0·8°
C(2)–C(1)–O(1)	117·0	0·5
C(2)–C(1)–O(2)	115·9	0·5
O(1')–O(5)–O(3')	107·1	0·4
O(2')–O(5)–O(4')	106·3	0·5
O(6₁)–O(6)–O(2')	118·2	0·4
O(2')–O(6)–O(4')'	109·6	0·5

* See footnote, Table 3.

The oxalate ion has at least a basic symmetry of $2mm$, its planarity being indicated by the 360·0° sum of the angles about the carbon atom and the bisecting symmetry plane. Within the limits of error, the ion may also be considered to have the symmetry mmm, the differences between corresponding bond lengths and angles (Fig. 3) not being statistically significant.

The fractional water atom, O(7), is not closely related with any other atoms. Its closest neighbor is the symmetry (m) related atom, O(7'), $3·06 \pm 0·12$ Å away. Its next closest neighbor is another water oxygen, O(5'), $3·11 \pm 0·04$ Å removed. The third nearest neighbor is an oxalate oxygen atom, O(2'), $3·29 \pm 0·01$ Å distant. Although it would seem that a closer bonding between O(7) and any of these other oxygen atoms could occur in a random manner, the data did not support a displacement of O(7) from the fourfold axis.

Discussion

The oxalate ion has been assigned different symmetries, according to the compounds in which it occurs and the accuracy of the data from which its configuration has been derived. In oxalic acid its symmetry is reportedly mmm (Zachariasen, 1934), but Ahmed & Cruickshank (1953) indicate the symmetry as $2/m$. In various salts, it has been shown to be closer to $2/m$ (Hendricks, 1935; Jeffrey & Parry, 1954). However, Fujita, Nakamoto & Kobayashi (1957) assumed that the angles were incor-

rect in the data of Jeffrey & Parry (1954) and that the ion symmetry is really mmm. The bound oxalate ion of Niekerk & Schoening (1951) was given the symmetry $2mm$ by Fujita *et al.* (1957). The oxalate ion of some salts may be non-planar (Hendricks & Jefferson, 1936; Griffith, 1943; Jeffrey & Parry, 1952). In whewellite (calcium oxalate monohydrate), Cocco & Sabelli (1962) described two different oxalate ions in the asymmetric unit. One ion may have the symmetry $2/m$ or mmm and the other $2/m$. Their data are not accurate enough to decide this point. In all probability, the true symmetry of the oxalate ion in weddellite is mmm, the environments of any pair of opposed sides of each oxalate group being essentially alike.

Hydrogen bonding would seem to be possible in several directions, according to O–O distances and O–O–O angles. Unfortunately, the hydrogen atoms are not available to help in the determination of the bonds. The pair of bonds O(5)–O(1') and O(5)–O(3') probably can be ruled out because the hydrogen atoms would be too close to the calcium atom. Thus O(5)–O(2') and O(5)–O(4') are likely hydrogen bonds about the water molecule at O(5). With O(6), there may be either the pair of bonds O(6)–O(2'), O(6)–O(4') or one of these two, together with O(6)–O(6₁). The latter set seems preferable on the basis of linking whole cells together, but the angle, O(6₁)–O(6)–O(2'), is somewhat larger than might be desired (Table 4). No good hydrogen-bonding relationship seems reasonable with the fractional water atom at O(7).

The data show that the crystal of weddellite has a basic hydrate content of 2 moles of water per mole of calcium. A fractional additional amount may be held, zeolitically, up to half a mole of water per mole of calcium. The maximum hydrate content can thus be 2·5 H_2O/Ca. This result accords with the findings of Philipsborn (1952).

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

BANNISTER, F. A. & HEY, M. H. (1936). *Discovery Reports,* **13**, 60.

COCCO, G. & SABELLI, C. (1962). *Atti Soc. Tosc. Sci. Nat. Ser. A,* **69**, 289.

FREY-WYSSLING, A. (1935). *Die Stoffauscheidung der höheren Pflanzen.* Berlin: J. Springer.

FUJITA, J., NAKAMOTO, K. & KOBAYASHI, M. (1957). *J. Phys. Chem.* **61**, 1014.

GASSER, G., BRAUNER, A. & PREISINGER, A. (1956). Z. Urol. **49**, 148.

GRIFFITH, R. L. (1943). J. Chem. Phys. **11**, 499.

HENDRICKS, S. B. (1935). Z. Kristallogr. (A) **91**, 48.

HENDRICKS, S. B. & JEFFERSON, M. E. (1936). J. Chem. Phys. **4**, 102.

HONEGGER, R. (1952). Inaug.-Dissert. Zürich.

JEFFREY, G. A. & PARRY, G. S. (1952). J. Chem. Soc., p. 4864.

JEFFREY, G. A. & PARRY, G. S. (1954). J. Amer. Chem. Soc. **76**, 5283.

KLASENS, H. A., PERDOK, W. G. & TERPSTRA, P. (1937). Z. Kristallogr. (A) **96**, 227.

NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1951). Acta Cryst. **4**, 35.

PHILIPSBORN, H. VON (1952). Protoplasma, **41**, 415.

POBEGUIN, T. (1943). Ann. Sci. Nat. Bot. XI, **4**, 1.

PRIEN, E. L. & FRONDEL, C. (1947). J. Urol. **57**, 949.

STERLING, C. (1964). Acta Cryst. **17**, 1224.

WALTER-LÉVY & LANIEPCE, J. (1962). C. R. Acad. Sci., Paris, **254**, 1073.

ZACHARIASEN, W. H. (1934). Z. Kristallogr. **89**, 442.

Optical Properties
and Preliminary X-Ray Investigation of Retamine and its Bromide and Chloride

BY J. M. BOSCH-FIGUEROA, L. MIRAVITLLES MILLÈ AND M. FONT-ALTABA

Crystallographic Department, C.S.I.C., University of Barcelona, Barcelona, Spain

The morphological, optical and X-ray properties of retamine and its bromide and chloride have been determined. These compounds crystallize in the enantiomorphic monoclinic class, space group $P2_1$; they are biaxial positive with optical axial angles of 66° and 77° respectively. The bromide and chloride are isomorphous.

Introduction

Retamine, an alkaloid contained in *Genista sagittalis*, was isolated and studied by Prof. Ribas Marquès and his collaborators of the Department of Organic Chemistry at the University of Santiago de Compostela (Spain) (see *e.g.* Ribas Marquès, 1961; Font-Altaba, 1957; Bosch-Figueroa, 1963). The molecules of retamine and sparteine have similar structures, which differ only in the presence of a hydroxyl group in position 7 or 9; this is indicated by hydrogenation of retamine, which produces sparteine and not α- or β-isosparteine.

Morphological and optical properties

Retamine and its bromide and chloride appear as colourless enantiomorphic crystals of tabular habit with a very simple combination of forms.

Retamine bromide presents the better crystals, with {100} as the predominant form, which confers on them a tabular habit (Fig. 1).
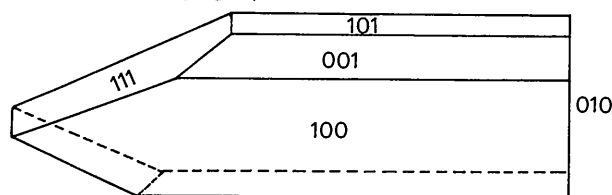

Fig. 1. Crystal of retamine bromide.

Crystals of retamine are of very varied size and thickness, very frequently with rounded edges and very rarely in quadrangular shapes. They lie frequently on the face ($\bar{1}01$).

Retamine chloride forms small crystals, and this makes its study difficult.

As retamine chloride is isomorphous with retamine bromide, we give in Table 1 the optical properties, and morphological and crystallographic data only of retamine and its bromide.

Table 1. *Morphological data of retamine and retamine bromide*

	Retamine			Retamine bromide	
hkl	φ	ϱ	hkl	φ	ϱ
001	90°0′	15°07′	100	90°0′	90°0′
$\bar{1}$01	270 0	28 48	010	0 0	90 0
011	11 15	54 08	001	90 0	10 38
$\bar{1}$00	270 0	90 0	$\bar{1}$01	270 0	31 27
			$\bar{1}1\bar{1}$	223 33	41 35
a:b:c:	1·7137	:1:1·3565	a:b:c:	0·81704	:1:0·6440
β	105°07		β	100°38	

By means of the polarizing microscope and the universal stage the orientation of the optical ellipsoid was determined. Refractive indices were measured by the immersion method. The results are shown in Table 2. Stereographic projections of retamine and retamine bromide are shown in Fig. 2.