

The crystal structure of calcium oxalate trihydrate: $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$

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Abstract

The crystal structure of calcium oxalate trihydrate, grown on whitlockite by reaction with oxalic acid, was determined utilizing 697 independent reflections and converged to $R = 0.034$. Important parameters are triclinic space group $P\bar{1}$, a 7.145(6), b 8.600(7), c 6.099(5), α 112.30(5), β 108.87(5), γ 89.92(5), with $2\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$ in the unit cell.

The structure is based on dimers of edge-linked square antiprisms of composition $\infty\text{Ca}_2\phi_{14}$ where ϕ = oxygen ligand which is linked to oxalate groups or water molecules to form a sheet parallel to $\{100\}$. In weddellite, square antiprisms link to form a $\infty[\text{Ca}_2\phi_{12}]$ chain and in whewellite a related polyhedron of order 8 links to form a $\infty[\text{Ca}_2\phi_{10}]$ sheet. It is not topologically possible to construct the series of structures by condensation of polyhedra alone since in each case some rearrangement of the water molecules is necessary.

Introduction

Not until recently (Walter-Levy and Laniece, 1962; Gardner, 1975) has there been agreement on the existence of a triclinic hydrate of calcium oxalate, characterized by three (or $2.5 < x < 3.0$) crystallographically non-equivalent water molecules. Contrary to whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite [$\text{CaC}_2\text{O}_4 \cdot (2 + x)\text{H}_2\text{O}$], calcium oxalate trihydrate [$\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$] is neither a major constituent of human urinary calculi nor a phase in sediments or plant metabolism. Nevertheless, there is growing speculation and some evidence (Tomazič and Nancollas, 1979) that $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$ could be a precursor to weddellite and whewellite formation. Evidently no structural study of $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$ has thus far materialized, apparently due to the difficulty of finding single crystals of quality and size amenable to structural work. Consequently, no analysis of the topogeometrical relationship—if any—between the

structure of calcium oxalate trihydrate and those of weddellite (Tazzoli and Domeneghetti, 1980), and whewellite (Tazzoli and Domeneghetti, 1980; Deganello and Piro, 1980) is available. Recently, however, we have succeeded in synthesizing sizeable—though somewhat warped—crystals of $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$. In this paper the crystal structure of calcium oxalate trihydrate is established and some of the relationships between the structures of the hydrates of calcium oxalate are pointed out.

Experimental

Crystals were grown by soaking massive whitlockite in oxalic acid solution for a week. At first, the crystals were believed to be another phase. They are colorless and exhibit a prismatic habit, tabular $\{100\}$. A long, thin crystal was repeatedly broken to obtain a suitable fragment, after several trial precession photographs to evaluate mosaic spread. It was aligned on a four-circle automated Picker FACS-1 diffractometer and intensities were collected by the θ - 2θ scan technique. Table 1 shows pertinent experimental details. Because of peak-splitting effects involving

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Table 1. Crystal and diffraction data for $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$

Property	Calcium oxalate Trihydrate
Formula	$\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$
$a(\text{Å})$	7.145(6)
$b(\text{Å})$	8.600(7)
$c(\text{Å})$	6.099(5)
$\alpha(^{\circ})$	112.30(5)
$\beta(^{\circ})$	108.87(5)
$\gamma(^{\circ})$	89.92(5)
Space group	$P\bar{1}$
Z	2
Crystal dimensions (mm)	$0.07 \times 0.10 \times 0.18$
Radiation (Å)	$\text{MoK}\alpha$, $\lambda = 0.71069$
Monochromator	graphite
$\mu(\text{cm}^{-1})$	9.3
Scan width ($^{\circ}$)	2.0
Scan speed (min^{-1})	$1^{\circ} \text{ min}^{-1}$
2θ range ($^{\circ}$)	0-45
Maximum $(\sin\theta)/\lambda$	0.538
Measured reflections	1348
Observed reflections, $I \geq 3\sigma(I)$	697

some high angle reflections and the small size of the crystal, only a limited data set was collected. No absorption correction was carried out owing to small crystal size and low linear absorption coefficient. After data reduction and correction for Lorentz and po-

larization effects, four atomic sites were deconvoluted from a Patterson synthesis, calculated with the programs assembled by Frenz (1972). Fourier and full-matrix least-squares analyses allowed unambiguous determination of all nonhydrogen atoms. With anisotropic refinement of the temperature factors the conventional R reduced to 0.036. Scattering factors for neutral Ca, O, and C were taken from *International Tables for X-ray Crystallography* (1974). No anomalous scattering correction was applied. The values of the atomic coordinates and temperature factors are listed in Table 2 and Table 2a lists the observed and calculated structure factors.²

The $\text{Ca}\phi_8$ polyhedra

The structures of $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$, $\text{Ca}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)$ and $\text{Ca}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)$, here written to stress coordination of (H_2O) and the oxalate group (C_2O_4) to Ca^{2+} , can be considered as progressive condensations of oxygen (ϕ) coordination polyhedra of order 8 about the Ca atom. Since there exist 257 polyhedra of order 8 (Britton and Dunitz, 1973) we utilized their tables to distinguish the kinds of polyhedra which constitute the structures. Two structures, the dihydrate and the trihydrate, correspond to poly-

² To obtain a copy of Table 2a, order Document AM-81-164 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 2. Calcium oxalate trihydrate: atomic coordinate and anisotropic thermal parameters ($\times 10^4$)*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.2810(1)	0.3079(1)	0.2161(2)	110(2)	58(2)	127(3)	2(1)	50(2)	26(2)
C(1)	-0.4015(6)	0.0501(6)	0.1082(8)	124(13)	100(10)	297(22)	-11(9)	64(13)	25(12)
O(1)	-0.4113(4)	0.1936(3)	0.2612(5)	138(8)	86(6)	334(15)	1(5)	49(8)	-44(8)
O(2)	0.2479(4)	0.0225(4)	-0.1109(5)	119(8)	106(6)	342(15)	10(6)	60(9)	-10(8)
C(2)	0.4285(6)	0.4439(5)	-0.1331(7)	105(11)	82(8)	184(18)	-8(8)	37(12)	38(10)
O(3)	0.2846(4)	0.3558(4)	-0.1421(5)	205(9)	198(7)	202(13)	-109(7)	38(9)	61(8)
O(4)	0.4643(4)	0.4484(3)	-0.3198(5)	153(8)	101(6)	157(11)	-26(5)	58(8)	42(6)
W(1)	0.1370(4)	0.1275(4)	0.3608(5)	141(9)	138(6)	187(13)	-46(6)	8(8)	47(8)
W(2)	0.1240(4)	-0.4439(4)	0.3688(6)	120(9)	116(6)	362(16)	12(6)	-8(9)	-14(8)
W(3)	0.0815(5)	-0.2452(4)	0.0550(6)	206(9)	129(6)	385(16)	4(6)	22(10)	91(8)
H(1)	0.014	0.434	0.646						
H(2)	0.803	0.345	0.487						
H(3)	0.865	0.325	0.853						
H(4)	0.989	0.101	0.313						
H(5)	0.211	0.165	0.540						
H(6)	0.823	0.136	0.808						

*Estimated standard errors in parentheses refer to the last digit. Coefficients in the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The isotropic B for the hydrogen atoms is 3.4 Å^2 .

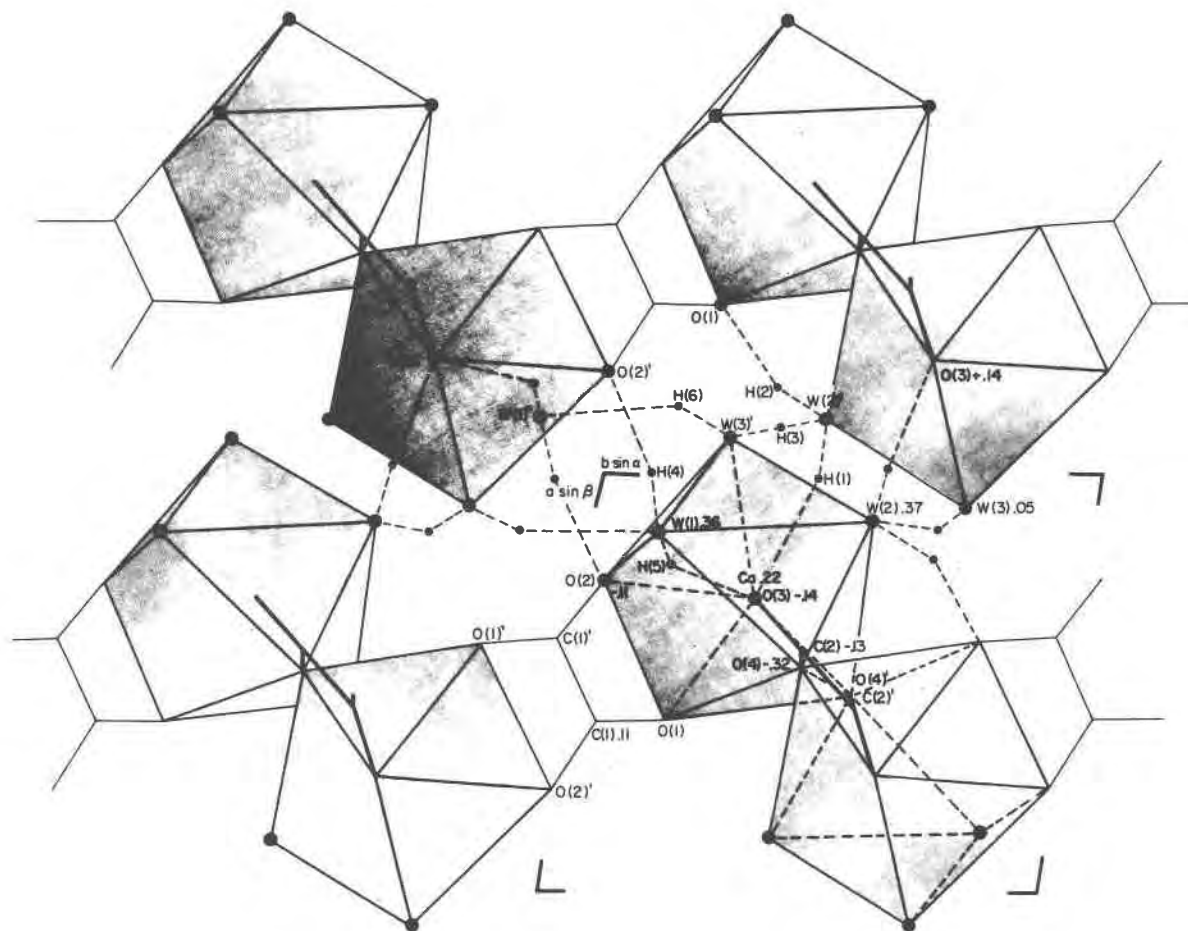


Fig. 1. Projection of $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$ down [001].

hedron No. 128 of Britton and Dunitz or, more familiarly, the square antiprism with maximal point symmetry D_{4d} ($8m2$). It consists of 16 edges comprised of two square and eight triangular faces. The monohydrate (whewellite) is more complex. Its polyhedron, No. 127, has maximal point symmetry $C_s(m)$ and also consists of 16 edges comprised of two square and eight triangular faces. However, in the latter polyhedron the squares are adjacent and share a common edge while in the square antiprisms they are opposed, linked by intervening triangles.

In $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$, shown as a polyhedral sketch in Figure 1, $\text{Ca}\phi_8$ square antiprisms link at common edges to form $[\text{Ca}_2\phi_{14}]$ dimeric groups. In each group the $\text{Ca}(\text{H}_2\text{O})_3\text{O}_5$ polyhedra possess H_2O (= W) molecules as groups of three on the vertices of a triangular face. Alternatively described, two of the water molecules define the edge of a square face, while the third is at a vertex of the remaining square face. The common polyhedral O(4)–O(4)' edge involves

oxygens associated with oxalate groups. The C(1)C(1)O₄ oxalate group, approximately in the plane of the projection, links to the $\text{Ca}\phi_8$'s by the O(1)–O(2). The C(2)C(2)O₄ oxalate group, approximately normal to the former group, links the $\text{Ca}\phi_8$'s

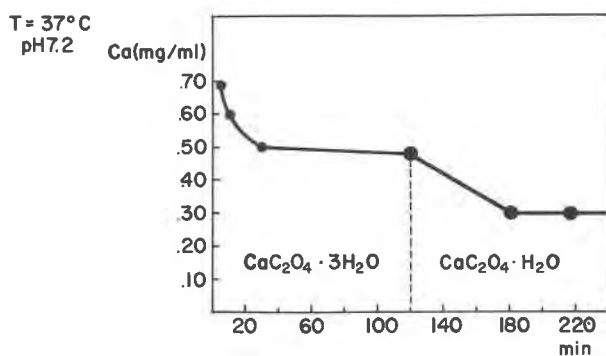


Fig. 2. The phase change calcium oxalate trihydrate-whewellite. Large black dots represent formation of whewellite.

Table 3. Selected interatomic distances (Å) and bond angles (°) in calcium oxalate trihydrate (standard deviations in parentheses)

Caφ ₈ polyhedron			
Ca-O(3)	2.380(3)	O(2)-O(3)	2.961(5)
-O(1)	2.384(3)	W(2)-W(3) [†]	2.963(4)
-W(2)	2.417(4)	O(1)-O(4)	3.000(5)
-W(1)	2.424(3)	O(1)-O(4) [†]	3.000(5)
-O(2)	2.458(4)	O(2)-W(1)	3.037(5)
-O(4)	2.489(4)	W(1)-W(3) [†]	3.046(5)
-W(3) [†]	2.508(4)	O(4)-W(2)	3.050(5)
-O(4) [†]	2.523(3)	O(3)-W(3) [†]	3.053(5)
average	2.448	O(2)-W(3) [†]	3.055(5)
		O(4)-W(1)	3.142(5)
O(3)-O(4)	2.670(4) [†]	O(1)-O(3)	3.443(5)
O(1)-O(2)	2.674(4) [†]	W(1)-W(2)	3.489(5)
O(4)-O(4) [†]	2.840(5)*	average	3.023
O(4)-W(2)	2.953(4)		
Oxalate units			
C(1)-C(1) [†]	1.551(8)	C(2)-C(2) [†]	1.534(7)
C(1)-O(1)	1.252(5)	C(2)-O(3)	1.253(5)
-O(2) [†]	1.260(5)	-O(4)	1.259(5)
average	1.256	average	1.256
Water molecules			
W(1)···O(2)	2.713(5)	W(1)···O(3) [†]	2.753(5)
W(1)-H(4)	1.00	W(1)-H(5)	0.97
H(4)-O(2)	1.78	H(5)-O(3) [†]	1.91
W(2)···O(3)	3.031(5)	W(2)···O(1) [†]	2.696(5)
W(2)-H(1)	0.96	W(2)-H(2)	0.95
H(1)-O(3)	2.22	H(2)-O(1) [†]	1.79
W(3)···W(1) [†]	2.983(5)	W(3)···W(2)	2.881(5)
W(3)-H(6)	1.04	W(3)-H(3)	1.04
H(6)-W(1) [†]	2.17	H(3)-W(2)	2.00
Oxalate angles			
O(1)-C(1)-O(2) [†]	126.9(4)	O(3)-C(2)-O(4)	126.2(4)
O(1)-C(1)-C(1) [†]	117.0(5)	O(3)-C(2)-C(2) [†]	115.5(5)

[†]Associated with an oxalate unit. *Shared edge between Caφ₈ polyhedra. Positions in Table 2 which are inverted are primed.

via O(4)-O(3) thus forming a completed linkage along [001]. It is admittedly not clear in the figure that O(3) and O(4) are associated with the next level up along [001], so that the Ca(1)φ₈'s are linked by the [C₂O₄]²⁻ "scissors" along $\bar{1}10$ and [001], thus defining a sheet parallel to {100} with the chain-like ... oxalate-Ca₂φ₁₄- ... component along [010] as

seen from Figure 1. Across this sheet is a network of hydrogen bonds whose hydrogen atoms are located from a difference Fourier synthesis. This results in the following bonds: O(2)-W(1)-O(3)', O(1)'-W(2)-O(3), W(2)-W(3)-W(1)'. Only the O(4)'s do not receive hydrogen bonds; these are the edge-sharing oxygens between the Caφ₈'s. From the structure we would infer that this network of hydrogen atoms should exercise a marked control over the physical properties of calcium oxalate trihydrate. Accordingly the plane of best cleavage should be along {100} and crystal growth and stability are expected to be enhanced in acid environments and at low temperatures. Upon heating, in fact, the increase in frequency of vibration of the acoustic modes in the lattice should favor coupling of intramolecular vibrations at the expense of weak intermolecular interactions such as those of the hydrogen bond. Direct experimental evidence supports the above. If calcium oxalate trihydrate is grown from equimolar solutions of calcium chloride and sodium oxalate at pH 7.2, it is noticed that crystal stability in the mother liquor is strongly temperature-dependent. For $T = 37^\circ\text{C}$ calcium oxalate trihydrate inverts to whewellite within 2 hours (Fig. 2); at 45°C , however, this phase change is almost instantaneous. For $T = 22^\circ\text{C}$ instead, the exchange to whewellite takes place in about 3 days. Conversely, at low temperature (12°C) calcium oxalate trihydrate grows reproducibly from solutions of calcium chloride and oxalic acid, only if the pH is ≤ 2 (Walter-Levy and Lanjepce, 1962). For higher pH values, whewellite forms. Such preferential exchange of calcium oxalate trihydrate to whewellite brings into perspective the role played by the water molecules. These, in all the three hydrates of calcium oxalate, not only complete the coordination of the Caφ₈ polyhedra but also act as effective structural stabilizers. In Ca(H₂O)₃(C₂O₄) the three waters define a face.

Table 4. Values of the unit-cell parameters for the hydrates of calcium oxalate

	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Space Group
Whewellite:							
Basic structure [†]	9.978(1) Å	7.295(1) Å	6.291(1) Å	90.0°	107.04(2)°	90.0°	<i>I</i> 2/ <i>m</i>
Derivative structure	9.9763(3)	14.5884(4)	6.2913(3)	90.0	107.03(2)	90.0	<i>P</i> 2 ₁ / <i>n</i>
Weddellite	12.371(3)	12.371(3)	7.357(2)	90.0	90.0	90.0	<i>I</i> 4/ <i>m</i>
Calcium oxalate trihydrate	7.145(6)	8.600(7)	6.099(5)	112.30(5)	108.87(5)	89.92(5)	<i>P</i> $\bar{1}$

[†]Basic structure and derivative structure refer to whewellite at high and low temperature, respectively, following the terminology proposed by Buerger (1947).

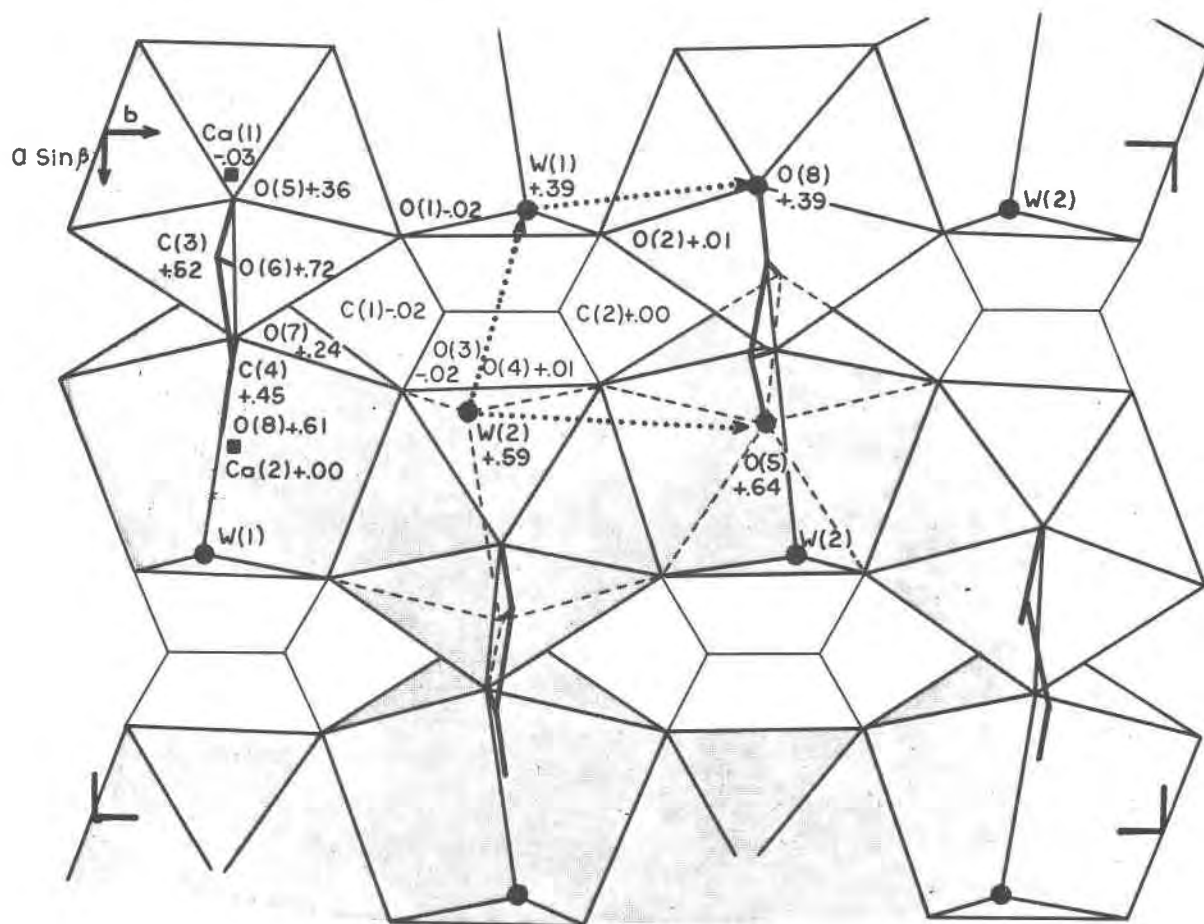


Fig. 3. Projection of whewellite down [001]. Note the sheet-like arrangement of the polyhedral linkages.

In weddellite, W(1) and W(2) in the $\text{Ca}(\text{H}_2\text{O})_2\text{O}_6$ polyhedron occur at face diagonals on a square. As for the monohydrate, W in the $\text{Ca}(\text{H}_2\text{O})\text{O}_7$ polyhedron is at the juncture of a triangular face and two square faces. Thus, from the standpoint of the water molecules alone, it is not topologically possible to proceed from one structure to the next by mere condensation of units already present since in each case some rearrangement of the water molecule distribution is necessary. These particularly interesting similarities arise when the structures of calcium oxalate trihydrate, weddellite, and whewellite are compared. To ease the task, pertinent unit cell values are reported in Table 4 while polyhedral diagrams and associated oxalate units are features in Figures 3, 4, and 5. Projections were selected emphasizing the dispositions of the oxalate groups. The best projections for comparison appear to be those which approximately show the oxalate groups arranged alternately in the plane and normal to the plane of projection.

This corresponds to [100] (in the $P2_1/a$ setting) and [010] for whewellite and weddellite, respectively. Figure 3 emphasizes the sheet-like arrangement of the polyhedral linkages of whewellite. We here defer from a detailed discussion of the structure of the latter, to point out that two nonequivalent $\text{Ca}(1)\phi_8$ and $\text{Ca}(2)\phi_8$ polyhedra link to form ${}^\infty[\text{Ca}_2\phi_{10}]$ sheets. Knitting of the $\text{Ca}(1)\phi_8$ and $\text{Ca}(2)\phi_8$ polyhedra is completely by two independent oxalate groups $\text{C}(1)\text{C}(2)\text{O}_4$ and $\text{C}(3)\text{C}(4)\text{O}_4$ approximately normal to one another. This arrangement of the $\text{Ca}(1)\phi_8$ - $\text{Ca}(2)\phi_8$ fragments is remarkably similar to the dimeric calcium oxalate trihydrate groups best seen along $[\bar{1}\bar{1}0]$ in Figure 1. Not only is there a water-water correlation in both structures but a remarkable correspondence between the $\text{C}(3)\text{C}(4)\text{O}_4$ oxalate groups of one with the $\text{C}(2)-\text{C}(2')\text{O}_4$'s of the other. The phase change calcium oxalate trihydrate-whewellite would thus appear crucially contingent to a positional shift of the $\text{C}(1)\text{C}(1')\text{O}_4$ oxalate group

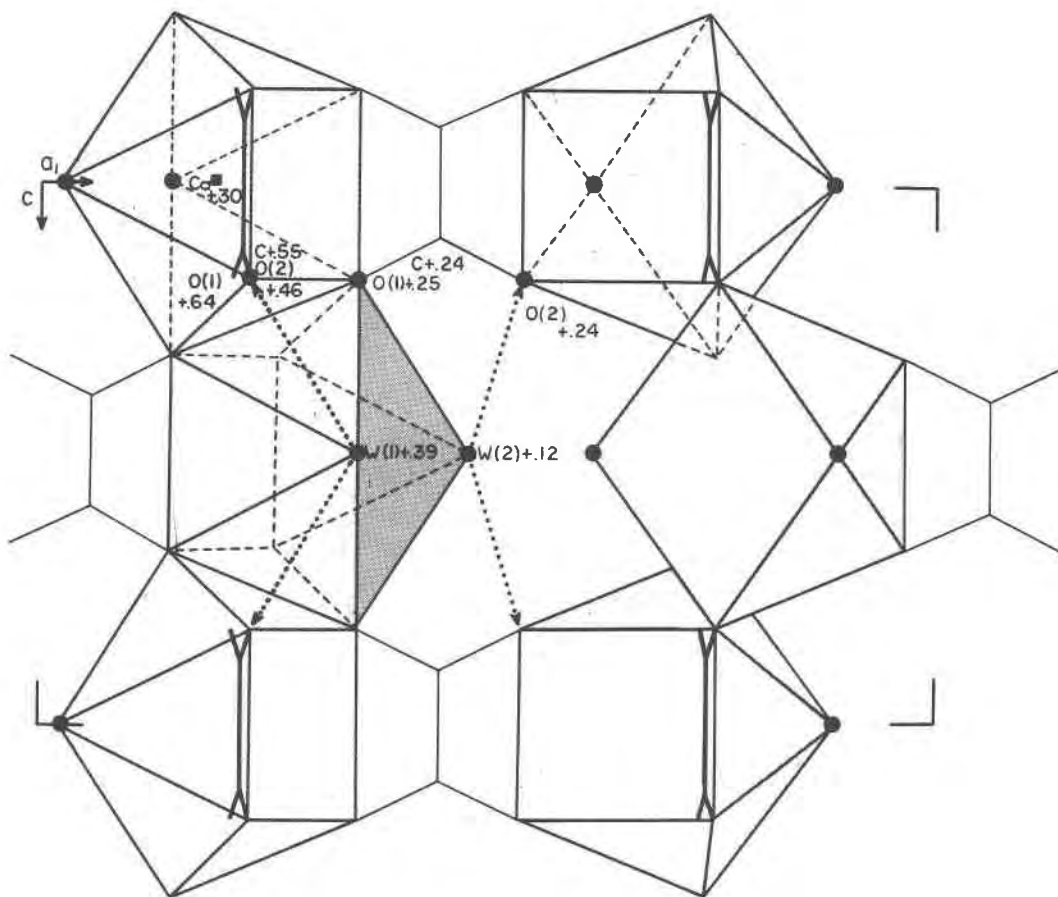


Fig. 4. Projection of weddellite down [010].

from the O(1)–O(2) edges in the trihydrate to the O(1)–O(2) and O(3)–O(4) links assumed in whewellite. A comparison between whewellite and weddellite is equally suggestive. Deferring from a more detailed discussion of the latter, we here point out that $\text{Ca}\phi_8$ square antiprisms link by shared edges to form $\frac{1}{2}[\text{Ca}_2\phi_{12}]$ chains parallel to [001]. Unlike $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)_2$, two oxalate “scissors” are associated with two edges of a square, the remaining square being defined by two water molecules and two corner-linked oxalate oxygens in *trans*-configuration. Analytically, the problem of reconstruction of one structure from the other was facilitated once it was realized that at 20°C whewellite possesses a superstructure (Deganello, 1980a). In whewellite upon ordering below 50°C, the value of *b* doubles because of the presence of very weak reflections with *k* odd. This results in a change of space group from $I2/m$ to the $P2_1/n$ (or $P2_1/c$) configuration usually reported.

Solution of the structure of whewellite at high temperature (Deganello, 1980b) provided the coordinates used in Table 5 to generate the atomic parameters of weddellite. The analysis here is deliberately restricted to the *y* and *z* coordinates including all but one atom because there is substantial misfit in the value of the unit cells of whewellite and weddellite along *a* (see Table 4). The transformation matrix from whewellite to weddellite is $y(\text{whew}) \rightarrow z(\text{wed})$; $2z(\text{whew}) \rightarrow y(\text{wed})$. Diagrammatically the overall similarities between the two structures may be appreciated in the Figure 5 series.

Acknowledgments

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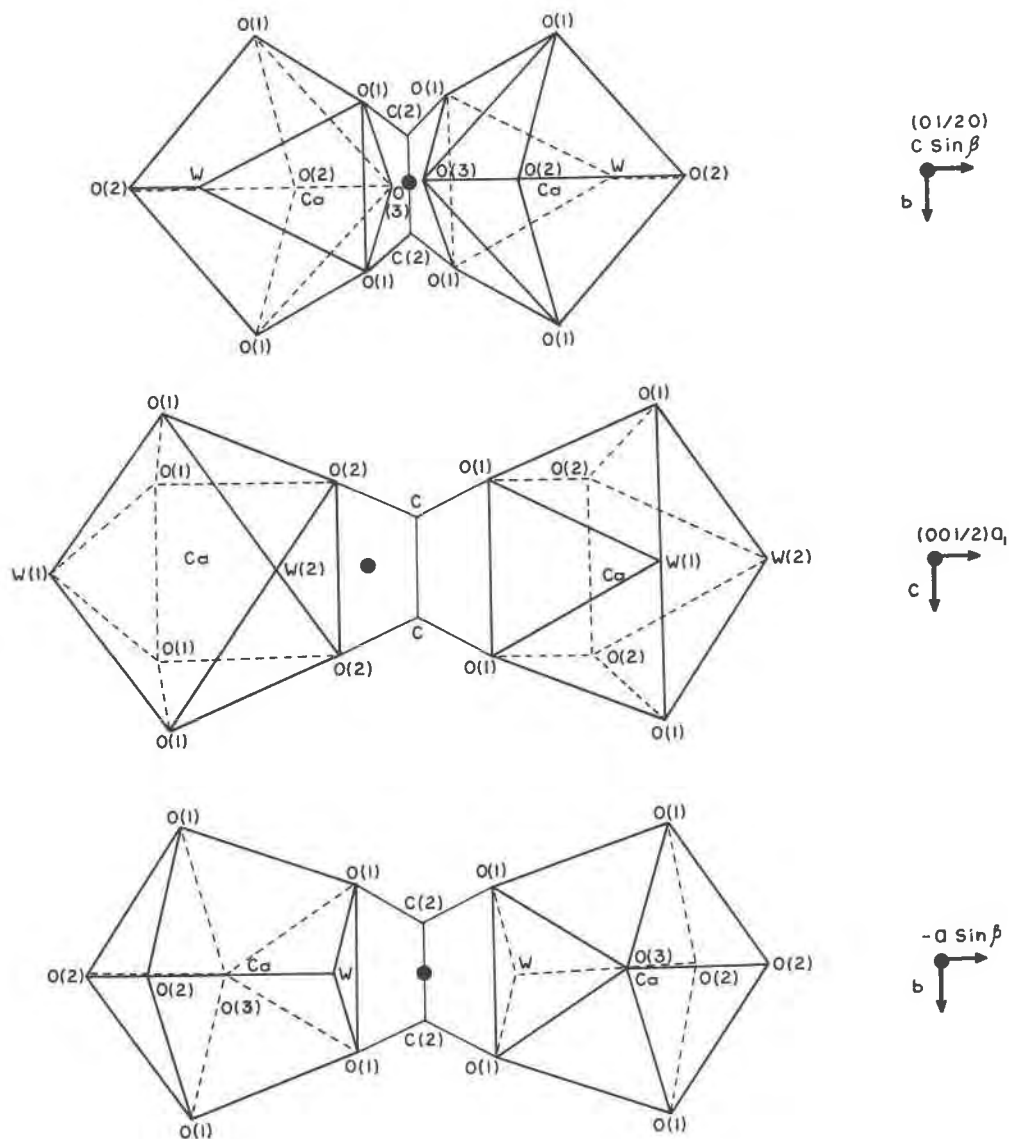


Fig. 5. Comparison between the polyhedral units in "basic" whewellite (top and bottom) with those in weddellite (middle).

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