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The crystal structure of calcium oxalate trihydrate: $Ca(H_2O)_3(C_2O_4)$

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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 $2Ca(H_2O)_3(C_2O_4)$ in the unit cell.

The structure is based on dimers of edge-linked square antiprisms of composition $^{0}_{\infty}Ca_2\phi_{14}$ 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 $^{1}_{\infty}[Ca_2\phi_{12}]$ chain and in whewellite a related polyhedron of order 8 links to form a $^{2}_{\infty}[Ca_2\phi_{10}]$ 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 Laniepce, 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 ($CaC_2O_4 \cdot H_2O$) and weddellite [$CaC_2O_4 \cdot (2 + x)H_2O$], calcium oxalate trihydrate [$Ca(H_2O)_3(C_2O_4)$] 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 $Ca(H_2O)_3(C_2O_4)$ could be a precursor to weddellite and whewellite formation. Evidently no structural study of $Ca(H_2O)_3(C_2O_4)$ 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 $Ca(H_2O)_3(C_2O_4)$. 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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K= -9

H	L	FOBS	FCALC
-1	2	10	9
-1	3	8	8
0	2	11	11
0	3	9	10
1	2	8	9
1	3	4	2

K= -8

H	L	FOBS	FCALC
-3	2	13	14
-3	4	9	10
-2	2	8	8
-2	3	5	5
-2	4	15	15
-1	1	14	15
-1	2	8	8
-1	3	9	9
-1	4	10	11
0	1	7	7
0	2	7	7
0	3	5	5
0	4	18	17
1	1	6	6
1	2	6	7
1	3	6	6
1	4	12	12
2	1	10	9
2	2	8	8
2	3	10	10
2	4	17	17
3	1	9	9

K= -7

H	L	FOBS	FCALC
-4	1	9	10
-4	3	7	7
-4	4	11	11
-3	1	7	7
-3	2	18	18
-3	3	10	10
-3	4	16	16
-2	1	12	12
-2	2	16	16
-2	3	7	8
-2	4	19	18
-1	1	9	9
-1	2	11	12
-1	3	7	8
-1	4	10	10
0	1	5	6
0	2	5	5
0	3	10	10
0	4	8	8
1	1	15	16
1	2	16	16
1	3	6	6
1	4	14	14
2	1	10	10
2	2	16	16
2	3	11	11
2	4	14	14
3	1	7	7

K= -6

H	L	FOBS	FCALC
-5	1	11	12
-5	2	6	6
-5	3	4	3
-4	1	4	4
-4	2	18	19
-4	3	15	15
-4	4	11	12
-3	1	12	14
-3	2	8	9
-3	3	16	15
-3	4	5	5
-2	1	20	20
-2	2	8	7
-2	3	21	21
-2	4	10	10
-1	1	5	6
-1	2	14	14
-1	3	18	19
-1	4	9	9
0	1	7	7
0	2	14	14
0	3	7	7
0	4	10	10
1	1	7	7
1	2	13	13
1	3	9	9
1	4	10	10
2	1	9	9
2	2	10	10
2	3	9	9
2	4	11	11
3	1	6	6
3	2	11	11
3	3	7	7
3	4	12	12

K= -5

H	L	FOBS	FCALC
-6	2	9	9
-6	3	22	22
-6	4	8	8
-5	1	7	6
-5	2	13	13
-5	3	5	5
-5	4	9	10
-4	1	11	10
-4	2	5	8
-4	3	8	6
-4	4	17	17
-3	1	7	7
-3	2	20	21
-3	3	4	4
-3	4	22	22
-2	1	11	11
-2	2	15	15
-2	3	6	5
-2	4	16	16
-1	1	18	18
-1	2	25	25
-1	3	16	16
-1	4	14	14
0	1	10	9
0	2	5	4
0	3	10	10
0	4	8	8
1	1	22	22
1	2	7	7
1	3	24	24
1	4	13	13
2	1	9	9
2	2	14	14
2	3	19	19
2	4	25	26
3	1	5	5
3	2	16	16
3	3	13	13
3	4	30	30
4	1	13	13
4	2	24	24
4	3	7	8
4	4	20	20
5	1	11	12
5	2	8	8
5	3	16	16
5	4	8	8
6	1	10	10
6	2	13	13
6	3	12	12
6	4	6	8

K= -4

H	L	FOBS	FCALC
-6	2	19	19
-6	3	10	9
-6	4	14	14
-5	1	10	11
-5	2	15	15
-5	3	5	6
-5	4	21	21
-4	1	8	8
-4	2	17	18
-4	3	9	9
-4	4	12	11
-3	1	3	2
-3	2	6	6
-3	3	7	8
-3	4	4	6
-2	1	15	15
-2	2	5	6
-2	3	20	20
-2	4	6	8
-1	1	10	9
-1	2	6	6
-1	3	17	17
-1	4	32	32
0	1	16	16
0	2	33	32
0	3	5	5
0	4	13	13
1	1	7	7
1	2	47	47
1	3	5	5
1	4	11	11
2	1	29	29
2	2	10	10
2	3	14	14
2	4	12	12
3	1	9	8
3	2	23	23
3	3	18	18
3	4	8	8
4	1	14	14
4	2	13	13
4	3	10	10

K= -3

H	L	FOBS	FCALC
-7	4	10	10
-6	1	14	14
-6	2	5	5
-6	3	14	14
-6	4	3	3
-5	1	17	17
-5	2	9	9
-5	3	6	5
-5	4	10	9
-4	1	11	11
-4	2	32	32
-4	3	17	16
-4	4	6	6
-3	1	17	17
-3	2	7	7
-3	3	8	8
-3	4	7	8
-2	1	17	17
-2	2	41	40
-2	3	49	49
-2	4	24	24
-1	1	14	13
-1	2	20	20
-1	3	14	14
-1	4	35	36
0	1	8	8
0	2	15	15
0	3	8	7
0	4	7	7
1	1	18	18
1	2	14	14
1	3	11	11
1	4	4	4
2	1	14	14
2	2	7	7
2	3	32	32
2	4	12	12
3	1	21	22
3	2	25	25
3	3	4	4
3	4	8	8
4	1	15	16
4	2	11	11
4	3	7	8
4	4	4	4

K= -2

H	L	FOBS	FCALC
-7	2	17	16
-7	3	20	20
-7	4	8	7
-6	1	4	2
-6	2	6	6
-6	3	11	11
-6	4	21	21
-5	1	6	6
-5	2	17	17
-5	3	17	18
-5	4	12	12
-4	1	10	10
-4	2	14	14
-4	3	17	16
-4	4	5	4
-3	1	35	35
-3	2	7	7
-3	3	16	16
-3	4	11	9
-2	1	32	32
-2	2	12	13
-2	3	24	23
-2	4	7	6
-1	1	9	8
-1	2	28	28
-1	3	80	81
-1	4	22	21
0	1	17	17
0	2	6	7
0	3	15	17
0	4	30	29
1	1	9	9
1	2	28	28
1	3	19	19
1	4	22	22
2	1	14	14

K= 0

H	L	FOBS	FCALC
-7	2	6	6
-7	3	6	4
-6	1	24	24
-6	2	5	5
-6	3	16	15
-6	4	9	8
-5	1	4	5
-5	2	9	10
-5	3	15	16
-5	4	10	10
-4	1	13	13
-4	2	39	38
-4	3	6	5
-4	4	27	27
-3	1	8	7
-3	2	10	11
-3	3	13	12
-3	4	20	20
-2	1	8	9
-2	2	26	26
-2	3	47	47
-2	4	9	9
-1	1	21	21
-1	2	6	3
-1	3	7	8
-1	4	15	15
0	1	13	13
0	2	25	26
0	3	38	37

K= 1

H	L	FOBS	FCALC
-7	1	4	4
-7	2	6	6
-6	1	18	18
-6	2	16	17
-6	3	10	9
-6	4	8	7
-5	1	12	12
-5	2	20	20
-5	3	8	7
-5	4	20	19
-4	1	18	18
-4	2	5	5
-4	3	7	7
-4	4	10	10
-3	1	12	12
-3	2	13	13
-3	3	44	44
-3	4	30	30
-2	1	16	16
-2	2	10	10
-2	3	19	20
-2	4	15	14
-1	1	22	22
-1	2	27	26
-1	3	9	10
-1	4	12	11
0	1	22	22
0	2	19	18
0	3	29	29
0	4	10	10
1	1	6	6
1	2	5	5
1	3	32	31
1	4	4	3
2	1	18	18
2	2	39	40
2	3	7	7
2	4	18	18
3	1	8	9
3	2	19	19
3	3	2	2
3	4	12	12
4	1	10	10
4	2	6	5
4	3	13	14
4	4	6	6

K= 2

H	L	FOBS	FCALC
-7	0	5	4
-7	1	4	3
-7	2	18	18
-7	3	4	2
-6	0	9	8
-6	1	10	10
-6	2	8	8
-6	3	12	12
-5	0	11	10
-5	1	6	6
-5	2	8	9
-5	3	7	7
-4	0	9	9
-4	1	11	12
-4	2	5	6
-4	3	18	18
-3	0	7	8
-3	1	9	9
-3	2	12	12
-3	3	5	5
-2	0	11	11
-2	1	15	15
-2	2	16	16
-2	3	6	5
-1	0	10	10
-1	1	23	24
-1	2	14	14
-1	3	9	9
0	0	6	6
0	1	32	32
0	2	33	33
0	3	5	5
1	0	11	11
1	1	15	15
1	2	16	16
1	3	6	5
2	0	7	7
2	1	17	17
2	2	17	16
2	3	8	8
3	0	8	8
3	1	20	20
3	2	8	8
3	3	4	4
4	0	4	4
4	1	6	6
4	2	7	7
4	3	4	4
5	0	5	5
5	1	6	6
5	2	5	5
5	3	4	4
6	0	6	6
6	1	7	7
6	2	6	6
6	3	4	4
7	0	4	4
7	1	4	4
7	2	4	4

K= 3

H	L	FOBS	FCALC
-7	0	7	7
-7	1	9	9
-6	1	16	16
-6	2	9	9
-6	3	11	11
-5	0	6	5
-5	1	10	10
-5	2	5	5
-5	3	12	12
-4	0	17	16
-4	1	20	20
-4	2	10	10
-4	3	10	9
-3	0	6	7
-3	1	38	38
-3	2	11	11
-3	3	10	10
-2	0	41	42
-2	1	29	30
-2	2	19	20
-2	3	17	17
-1	0	5	4
-1	1	12	13
-1	2	14	14
-1	3	14	14
0	0	50	51
0	1	29	29
0	2	7	6
0	3	27	27
1	0	12	12
1	1	19	19
1	2	12	12
1	3	42	42
2	0	6	6
2	1	6	5
2	2	5	5
2	3	9	9
3	0	10	9
3	1	30	30
3	2	4	4
3	3	13	12
4	0	17	16
4	1	18	18
4	2	4	6

K= 4

H	L	FOBS	FCALC
-6	0	16	17
-6	1	4	3
-6	2	7	7
-6	3	6	7
-5	1	19	18
-5	2	11	11
-5	3	20	20
-4	0	21	21
-4	1	7	6
-4	2	11	10
-4	3	4	4
-3	0	17	17
-3	1	20	20
-3	2	4	4
-3	3	24	23
-2	0	9	9
-2	1	5	5
-2	2	5	6
-2	3	18	17
-1	0	8	8
-1	1	20	19
-1	2	30	29
-1	3	12	13
0	0	4	4
0	1	13	14
0	2	17	16
0	3	18	18
1	0	4	6
1	1	30	30
1	2	12	13
1	3	13	12
2	0	10	10
2	1	6	6
2	2	5	5
2	3	6	6
3	0	5	5
3	1	6	6
3	2	6	6
3	3	4	4
4	0	4	4
4	1	4	4
4	2	4	4

H	L	FOBS	FCALC
-11	4	10	10
-11	5	6	6
-10	0	10	9
-10	1	13	13
-10	3	4	4
-10	4	8	8
-9	0	34	33
-9	1	9	8
-9	2	23	23
-9	3	8	9
-9	4	4	4
-8	0	11	11
-8	1	8	9
-8	2	14	15
-8	3	21	21
-8	4	8	9
-7	1	15	15
-7	2	14	13
-7	3	19	20
-7	4	4	2

K= 5

H	L	FOBS	FCALC
-5	0	18	18
-5	1	14	14
-5	2	15	15
-4	0	18	18
-4	1	8	8
-4	2	15	15
-4	3	7	7
-3	0	8	10
-3	2	10	11
-3	3	7	6
-2	1	16	16
-2	2	13	14
-2	3	17	16
-1	0	16	16
-1	1	22	21
-1	3	11	11
0	0	8	8
0	1	18	18
0	3	4	6
1	1	10	10
1	2	23	23
1	3	7	7
2	0	25	25
2	1	9	10
2	2	15	16
3	0	6	5
3	1	15	15
3	2	8	7
4	0	4	4
4	1	6	7
5	0	7	5

K= 6

H	L	FOBS	FCALC
-5	0	7	9
-5	1	8	8
-4	0	10	10
-4	1	17	17
-4	2	7	7
-3	1	4	1
-3	2	6	6
-2	0	5	3
-2	1	27	27
-2	2	9	10
-2	3	5	6
-1	0	20	19
-1	1	8	8
-1	2	12	13
0	0	7	7
0	1	7	7
1	0	8	8
1	2	9	10
2	0	27	27
2	1	20	21
3	0	11	11
3	1	14	14
4	0	5	6

K= 7

H	L	FOBS	FCALC
-4	0	11	12
-4	1	8	7
-3	0	14	13
-3	1	9	10
-2	0	10	9
-2	1	7	8
-1	0	12	12
-1	1	17	17
-1	2	5	7
0	0	12	12
0	1	8	9
1	0	10	10
1	1	13	13
3	0	8	8

K= 8

H	L	FOBS	FCALC
-3	0	8	8
-2	0	6	7
-1	0	15	14
0	0	15	15
1	0	7	7