moins que dans ces quatre structures la symétrie du coordinat est toujours $\bar{1}$ car coïncidant avec la centrosymétrie du groupe et qu'elle avoisine plus ou moins la symétrie $2/m$.

On peut souligner deux autres différences entre les deux complexes de l'argent. D'une part l'éthane-disulfonate d'argent(I) est, à notre connaissance, le premier complexe de l'argent(I) décrit où l'argent présente une telle distribution en couches. D'autre part dans ce complexe il y a deux distances Ag···Ag égales à la distance de liaison des atomes d'argent dans le métal pur (2,89 Å) alors que rien de tel n'est observé pour le butanedisulfonate. Il n'est pas encore possible, à ·notre avis, d'affirmer si cette distance, observée parfois dans les complexes de l'argent(I), correspond effective-ment à une liaison entre atomes d'argent.

Les calculs ont éte effectués sur ordinateur IBM 370-168 à Orsay (CIRCE) par l'intermédiaire du terminal de l'Institut de Recherches sur la Catalyse de Lyon et à l'aide d'une bibliothèque de programmes classiques organisée par H.Loiseleur au Laboratoire de Chimie Analytique 2 (Quaglieri, Loiseleur & Thomas, 1972).

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The Structure of Whewellite, $CaC_2O_4.H_2O$, at 328 K

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Abstract

At 328 K whewellite is monoclinic, space group $I2/m$, with $a = 9·978$ (1), $b = 7·295$ (1), $c = 6·292$ (1) Å, $\beta = 107·07$ (3)°, $Z = 4$. 373 intensities were collected by the θ–2θ scan technique (Mo $K\alpha$: $\lambda = 0·71069$ Å; 328 K), and the structure was refined to $R = 0·047$. There are two crystallographically non-equivalent oxalate ions, (I) and (II), in special position $2/m$, linking Ca-centered polyhedra. The C—O distances vary between 1·229 and 1·253 Å while individual Ca—O lengths are between 2·425 and 2·469 Å. The hydrogen-bond network appears to control the planarity of oxalate (I) as well as structural stability.

Introduction

Whewellite ($CaC_2O_4.H_2O$) is found in sediments, plants, animals, and is a major constituent of human urinary calculi. Whewellite, weddellite $[CaC_2O_4.(2 + x)H_2O$ with $x \leq 0·5]$ and calcium oxalate trihydrate ($CaC_2O_4.3H_2O$) have been generally accepted to represent the polymorphism of the hydrates of calcium oxalate. The crystal structure of whewellite was originally studied by Cocco (1962) and Cocco & Sabelli (1962), and recently reexamined by Tazzoli & Domeneghetti (1980) and Deganello & Piro (1981). The crystal structure of weddellite was proposed by Sterling (1965) and refined by Tazzoli & Domeneghetti (1980). The structure of calcium oxalate trihydrate has likewise recently been determined (Deganello, Kampf & Moore, 1981). Since then, the existence of yet another polymorph has been demonstrated (Deganello, 1980). Precession photographs of whewellite taken at high temperature showed the existence of both a basic* structure (stability range $\simeq$ 318–425 K) and a derivative structure (stability range $\simeq$ 293†–318 K). Transition from the former to the latter takes place

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* Since the high- and low-temperature form conform to the topogeometrical criteria discussed by Buerger (1947), the terminol-ogy, basic structure and derivative structure proposed by that author will be used in this paper.

† This figure is only indicative since no information is available regarding low-temperature work.

upon ordering below 318 K and is characterized by the appearance of very weak reflections with k odd. Because of these, the value of the cell edge b doubles with respect to its high-temperature counterpart, while the space-group symmetry changes from $I2/m$ to $P2_1/n$. This phase change is completely reversible. In this paper the structure of whewellite at 328 K is established as part of a study of the structural relationships between the hydrates of calcium oxalate.

Experimental

Crystals were grown from gels (Deganello & Piro, 1981). They are colorless and exhibit a prismatic habit [{010}, {001}, {110}, *etc.*]. To obtain intensities at high temperature, a heater similar to that described by Brown, Sueno & Prewitt (1973) was mounted on a Syntex $P2_1$ four-circle automated diffractometer. Graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) was used. The cell parameters at 325 K, calculated from powder data obtained with a Guinier–Lenné camera, are: $a = 9.978$ (1), $b = 7.295$ (1), $c = 6.292$ (1) Å, $\beta = 107.07$ (3)°,* $Z = 4$ for $D_o = 2.20$ and $D_c = 2.216$ Mg m^{-3}. Precession photographs taken in the temperature range 293–358 K with the same heater mounted on the diffractometer indicated space groups $I2/m$, $I2$ or Im ($h + k + l = 2n$). Intensities were collected at the same temperature used for the determination of the cell parameters, with the θ–2θ scan technique, using a crystal $0.08 \times 0.07 \times 0.03$ mm with c slightly offset from the φ axis of the diffractometer. The scanning rate was 1° with 20 s at the scan limits. After proper insulation of both the specimen (0.012 mm thick Kapton foil) and the entire goniostat assembly from outside currents, temperature stability was monitored to be within ±1 K. Two standard reflections, measured after every fifty data, consistently exhibited F values well within 1σ. After data reduction and correction for Lorentz–polarization effects, 414 independent intensities [$(\sin \theta/\lambda)_{max} = 0.55$ Å^{-1}] were converted into F's. Of these, 41 were discarded because of asymmetric backgrounds, and/or unreliable statistics [$I < 2\sigma(I)$] where σ is given by equation (H.14) of Stout & Jensen (1968). Absorption corrections ($\mu = 1.3$ mm^{-1}) were not carried out.

Determination of the structure

Deconvolution of a Patterson synthesis, calculated with the programs assembled by Frenz (1972), yielded the coordinates of Ca^{2+} and two O atoms. Fourier and

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* The derivative structure at 293 K is characterized by $a = 9.9763$ (3), $b = 14.5884$ (4), $c = 6.2913$ (3) Å, $\beta = 107.05$ (3)°; with space group $P2_1/n$ and $Z = 8$.

Table 1. *Fractional atomic coordinates with e.s.d.'s* ($\times 10^4$)

	x	y	z	B_{eq}* (Å^2)
Ca	0.1903 (1)	0.0	0.1751 (2)	0.97 (7)
O(1)	0.1105 (3)	−0.3157 (3)	0.1096 (4)	1.37 (12)
O(2)	−0.0493 (4)	0.0	0.2119 (7)	1.63 (16)
O(3)	−0.1783 (5)	0.0	0.4454 (9)	3.31 (22)
C(1)	−0.0652 (6)	0.0	0.3984 (9)	1.45 (24)
C(2)	0.0	0.3937 (8)	0.0	1.39 (23)
O(W)	−0.3552 (5)	0.0	0.0438 (8)	3.93 (24)
H(1)	0.45	0.0	0.04	
H(2)	−0.33	0.05	0.20	

$$* B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

full-matrix least-squares analysis allowed unambiguous determination of all non-hydrogen atoms, indicating $I2/m$ as the correct space group.* With isotropic temperature factors R was 0.10 and $R_w = 0.12$, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The H atoms, located from difference maps, were included but not refined in the anisotropic refinement. This converged to $R = 0.047$ and $R_w = 0.055$ with average and maximum parameter shifts, in fractions of the e.s.d.'s, of 0.02 and 0.05 respectively.

A final difference synthesis showed no anomalies. Scattering factors for Ca, O, C and H were taken from *International Tables for X-ray Crystallography* (1968). No anomalous-scattering correction was applied. Unit weight was assigned to each observation. Table 1 lists the atomic coordinates.†

Discussion

There are two crystallographically non-equivalent oxalate ions, both of which are planar and in special position $2/m$. One of them, (I), is bisected by a mirror plane normal to the C—C bond, which is located along the unique axis. The other, (II), is located on a mirror plane, and its C—C bond is bisected by a twofold crystallographic axis. The orthogonal relationship of these two ions with respect to one another (Figs. 1, 2) results in two distinct types of planar packing. (I) generates, together with the Ca^{2+} ions, a layering sequence along ($\bar{1}01$), which repeats itself according to a unit translation along c. The layers are interlocked by (II) ions and water molecules. Eight O atoms, located

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* The equivalent positions in $I2/m$ are: x,y,z; $\bar{x},y,z$; $\tfrac{1}{2} + x, \tfrac{1}{2} + y, \tfrac{1}{2} + z$; $\tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$; $x,\bar{y},z$; $\bar{x},\bar{y},z$; $\tfrac{1}{2} - x, \tfrac{1}{2} - y, \tfrac{1}{2} - z$; $\tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} - z$.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35869 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
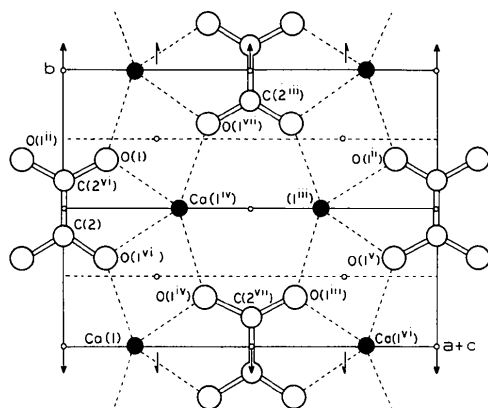
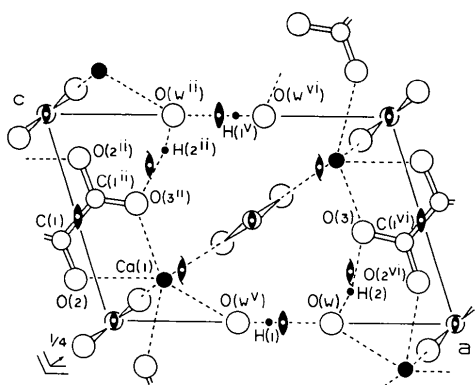Fig. 1. The layering sequence along (Ī01). Filled circles represent Ca atoms.

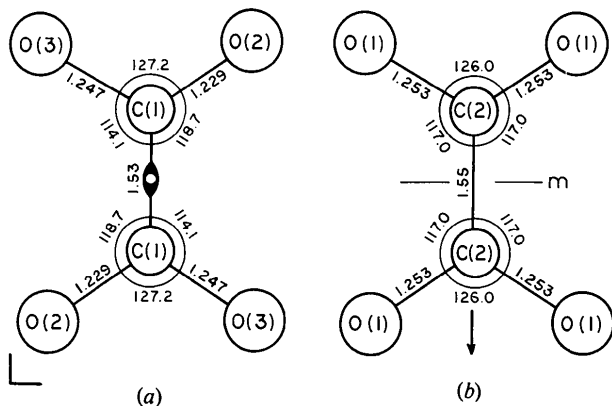Fig. 2. The packing along b. Filled circles represent Ca atoms.

(a)   (b)

Fig. 3. (a) Oxalate ion (I). Distances (Å) and angles (°) have average e.s.d.'s of 0·008 Å and 0·6°. (b) Oxalate ion (II). The average e.s.d.'s are 0·004 Å and 0·4°.

Table 2. Selected interatomic distances (Å)

Ca polyhedron

Ca—O(1)	2·432 (2)	O(1)—O(1)	2·984 (5)
Ca—O(1)	2·432 (2)	O(1)—O(2)	2·977 (4)
Ca—O(1)	2·452 (2)	O(1)—O(2)	3·007 (4)
Ca—O(1)	2·452 (2)	O(1)—O(3)	2·931 (6)
Ca—O(2)	2·429 (4)	O(1)—O(W)	2·973 (5)
Ca—O(2)	2·469 (4)	O(2)—O(2)	3·101 (9)
Ca—O(3)	2·425 (6)	O(2)—O(W)	2·922 (6)
Ca—O(W)	2·435 (6)		
Mean	2·441		

Carboxyl groups

O(3)—O(2)	2·218 (7)	O(1)—O(1)	2·232 (5)
O(3)—O(2)	2·634 (6)	O(1)—O(1)	2·688 (5)

Hydrogen bonds

O(W)—O(3)	2·624 (6)	O(W)—H(1)	1·89
O(W)—O(W)	2·778 (10)	O(W)—H(2)	1·01
O(W')—H(1)	0·98	O(3)—H(2)	1·85

water molecules, found at van der Waals contact distances, are hydrogen bonded to one another. The hydrogen-bond configuration is completed through the O(3)—O(W) interaction which minimizes electrostatic repulsions between (I) and the Ca polyhedron. Table 2 and Fig. 3 report interatomic distances and angles calculated with ORFFE (Busing, Martin & Levy, 1964).

The stability of this basic structure appears to depend on the water molecule. This performs a dual role: as a ligand it completes the coordination of the Ca sites while concomitantly acting as an effective structural stabilizer through hydrogen bonding. Upon heating at 425 K, however, there is enough thermal motion in the lattice to induce a phase transition to α-Ca_2CO_4. This was determined with powder data obtained with a Guinier–Lenné camera in the temperature range 293–458 K.

It would appear reasonable to assume that up to the temperature of the hydrous–anhydrous phase change, the (I) and (II) ions should retain, aside from increments due to thermal expansion, the stereochemistry found at 328 K. At this temperature the values of their interatomic distances and angles agree with those proposed by Hahn (1957) for the isolated $C_2O_4^{2-}$ ion. Furthermore, their specialized $2/m$ symmetry, attainable only above 318 K, suggests that a fair amount of phononic activation is necessary to promote conjugation effects leading to planarity of the ions. The process might be envisaged as the result of the increase in the frequency of vibration of the acoustic modes which occurs upon heating, favoring coupling of molecular vibrations in the lattice at the expense of weak intermolecular interactions, such as those of the hydrogen bond. Below 318 K, however, the magnitude of such an effect is expected to be minor: indeed, at 293 K the (I) ions, which are hydrogen bonded to water

at the corners of a distorted polyhedron, coordinate each Ca^{2+} ion. Seven of these O atoms are from the oxalate ions; the last belongs to a water molecule. Adjacent Ca-centered polyhedra are linked through edge sharing, with cation–ligand distances ranging from 2·425 to 2·469 Å. Pairs of symmetry-related

molecules, have symmetry 1 and are significantly non-planar according to standard statistical tests (Tazzoli & Domeneghetti, 1980; Deganello & Piro, 1981). It would thus appear that the hydrogen bond, in the absence of strong intramolecular vibrational coupling, may affect the balance between the repulsion of the carboxyl O atoms and the electronic configuration along the C—C bond.

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The Structure of Diaqua(N-salicylidene-L-threoninato)copper(II)

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Abstract

The structure of the Schiff-base-type complex diaqua-(N-salicylidene-L-threoninato)copper(II) $\{[Cu(C_{11}H_{11}NO_4)(H_2O)_2]$, $a = 6\cdot681$ (4), $b = 13\cdot640$ (8), $c = 14\cdot646$ (8) Å, $\beta = 90\cdot88$ (4)°, $Z = 4$, $V = 1335$ Å³, monoclinic, space group $P2_1\}$ has been solved by three-dimensional Fourier methods and refined by the block-diagonal least-squares technique, H atoms excluded, to an R value of $0\cdot070$ for 2324 reflections. The asymmetric unit consists of two complex units situated at a hydrogen-bond distance from each other. The coordination sphere around the Cu^{II} central atoms is slightly distorted square pyramidal (4 + 1). The basal planes consist of the tridentate N-salicylidene-L-threonine group and an O atom of a water molecule [in one complex unit Cu(1)–O(1) = 1·95 (1), Cu(1)–N(1) = 1·95 (1), Cu(1)–O(3) = 1·92 (1), Cu(1)–O(4) = 1·96 (1) Å; in the other, Cu(2)–O(7) = 1·98 (1), Cu(2)–N(2) = 1·93 (1), Cu(2)–O(9) = 1·92 (1), Cu(2)–O(10) = 1·97 (1) Å]. The axial positions are occupied by O atoms of the second water molecules [Cu(1)–O(5) = 2·42 (1) and Cu(2)–O(11) = 2·34 (1) Å]. The orientation of the 1-hydroxyethyl group of the threoninato residue is different in the two complex units. In one complex unit the hydroxyl O atom of this group points towards the axial water molecule and in the other it points away.

Introduction

Earlier, three structures of the transition-metal complexes derived from salicylaldehyde and amino acids were solved in this laboratory: catena-μ-(N-salicylidene-L-tyrosinato-O,O')-copper(II) (Hämäläinen,