cyclic ring have a mean value of 1·353 Å, in agreement with values reported in literature for such linkages. The methyl–oxygen distances in the methoxyl groups are regular, with a mean value of 1·442 Å.

The average C–H bond length is 1·11 Å. The distance between two oxygen atoms of adjacent methoxyl groups is 2·653 Å. The shortest intermolecular contacts are listed in Table 9.

References

ADEMBRI, G., DE SIO, F., NESI, R. & SCOTTON, M. (1969). *2me Congrés Int. de Chimie Heterocyclique, Montpellier,* p. 188.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
FRIEDEL, G. (1926). *Leçons de Cristallographie.* Paris: Blanchard (repr. 1964).
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
SABELLI, C., TANGOCCI, P. & ZANAZZI, P. F. (1969). *Acta Cryst.* **B25**, 2231.
SABELLI, C. & ZANAZZI, P. F. (1972). *Acta Cryst.* **B28**, 1173.
STEWART, J. M. (1964). Technical report TR-64-6, Computer Science Center, Univ. of Maryland.

The Crystal Structure of Devillite*

BY C. SABELLI

Centro di Geochimica e Cristallochimica del Minerali del C. N. R., Istituto di Mineralogia dell'Università di Firenze, Italy

AND P. F. ZANAZZI

Istituto di Mineralogia dell'Università di Perugia, Italy

Devillite, $CaCu_4(OH)_6(SO_4)_2.3H_2O$, is monoclinic, space group $P2_1/c$; with $a=20\cdot870$, $b=6\cdot135$, $c=22\cdot191$ Å, $\beta=102°44'$ and $Z=8$. The crystal structure was solved by means of three-dimensional Fourier methods, starting from the atomic arrangement found for serpierite, a mineral with close analogies with devillite. The refinement by the least-squares method yielded a final R index of 0·11 for 1485 reflexions. Each copper ion, in $4+2$ coordination, is linked by six edges to six adjacent copper ions forming sheets $^2_\infty[Cu_2(OH)_3O]^-$ parallel to (100). Two adjacent parallel sheets are connected by calcium ions in sevenfold coordination, by SO_4^{2-} tetrahedra, and by a system of hydrogen bonds. An interpretation of the complex twinning exhibited by the mineral is given. Analogies and differences with the structure of serpierite are discussed.

Introduction

Devillite is a rare hydrated basic copper calcium sulphate of formula $CaCu_4(OH)_6(SO_4)_2.3H_2O$, originally found in Cornwall (England) and first described by Pisani (1864). The mineral was later found in Hungary and studied by Březina (1879) as herrengrundite and independently by Szabo (1879), who named it urvölgyite. Meixner (1940) by comparison of chemical, optical and morphological data showed that these mineralogical species were identical.

The mineral is monoclinic; its lattice parameters were determined by Wappler (1965) who found the crystals to be one-dimensionally disordered and could not determine the space group. Faraone, Sabelli &

Zanazzi (1967) re-examined the mineral and pointed out the close relationship between devillite and serpierite. The crystal structure of the latter mineral was determined by Sabelli & Zanazzi (1968). In the present study the results of a crystal structure determination on devillite are reported, and the similarities, as well as the differences, in structural features of the two minerals are explained. The structural disorder in devillite is interpreted in terms of a complex twinning.

Experimental

A sample of devillite from Herrengrund (Hungary) was used for the present work. The crystals are thin bluish-green plates flattened on {001} and striated along [010]. The lattice parameters are $a=20\cdot870$ (2), $b=6\cdot135$ (2), $c=22\cdot191$ (3) Å, $\beta=102°44$ (1)', as determined in a previous paper (Faraone, Sabelli & Zanazzi,

---

1967) by application of the least-squares method to 2θ data obtained from Weissenberg photographs calibrated with the powder pattern from Ag. From systematic absences in reflexions, the space group was uniquely assigned as $P2_1/c$. In addition to the extinctions of this space group ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) reflexions with h odd when $k + l$ is even are absent. Assuming a cell content of 8 $CaCu_4(OH)_6(SO_4)_2.3H_2O$, the calculated density, 3·06 g.cm^{-3}, is in agreement with the experimental value 3·13 g.cm^{-3} reported by Palache, Berman & Frondel (1951).

Diffraction intensities from $h0l$ to $h4l$ reciprocal lattice layers were collected for the structural study, employing the Weissenberg equi-inclination technique and using Cu $K\alpha$ radiation. The existence of twinning

Fig. 1. The crystal structure of devillite projected along the b axis.

Fig. 2. A copper–oxygen sheet showing the arrangement of the 4+2 complexes. Black dots represent Cu ions, open circles oxygen atoms. Projection along the a axis.

greatly complicates the appearance of the photographs. They have a double lattice character and, furthermore, the reflexions with $k + l = 2n + 1$ are diffuse, the spread of reflexions taking place along the a^* reciprocal axis. This feature was common to all the crystals tested for collection of intensity data. The splitting of spots was attributed to the existence of two individuals, A and B, in each crystal, having a^* and b^* reciprocal lattice axes antiparallel and the c^* axes making an angle of $180°-2\beta^*$, $i.e.$ $25°28'$. According to Friedel's (1926) geometrical notation, devillite is twinned by pseudo-merohedry, with reflexion plane (100). The diffuse reflexions with $k + l$ odd may be attributed to a multiple twinning of the kind first found in serpierite crystals.

The intensities were evaluated with a microdensitometer; for the diffuse spots, they were measured at the reciprocal lattice points.

Because of twinning and of lattice geometry the $hk0$ and $hk24$ reflexions from the A individual overlap the $\bar{h}\bar{k}0$ and $h'\bar{k}24$ reflexions of the B individual, where $h' = h + 10$. It is then necessary to apply a correction to the superimposed intensity data. The correction was applied by Grainger's (1969) method, evaluating the twin fraction f (the ratio of the volume of one component to the total volume of the twin) using the same distinct reflexions arising from each of the individuals. The only allowance for the diffuse nature of the reflexions with $k + l$ odd was the separate rescaling of these data during the structure determination by comparing the observed with the relative calculated structure factors.

The usual geometrical factors, as well as an empirical correction for the α_1–α_2 doublet resolution, were applied. No absorption correction was made. A total of 2293 independent reflexions was recorded, 1485 of which were measurable. Different layers were placed on approximately the same relative scale by taking into account their exposure time; later, the scale factors were determined by comparing observed and calculated structure factors.
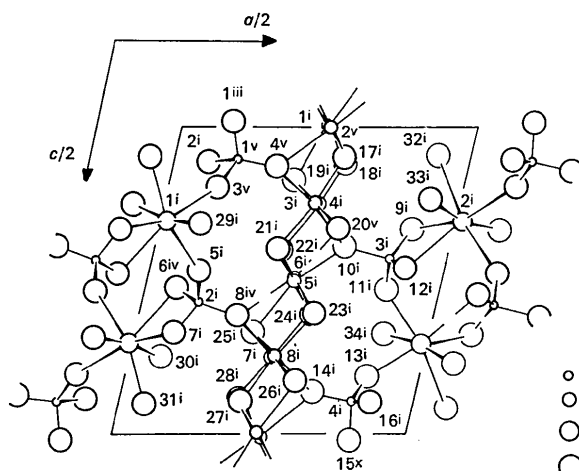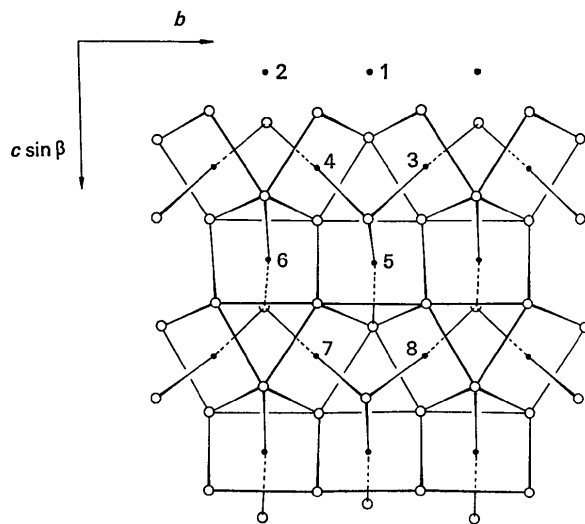
Structure determination and refinement

There are evident structural similarities between serpierite and devillite. $h0l$ Weissenberg photographs show that the two minerals have nearly the same value for the a^* period (0·04910 Å^{-1} in serpierite, 0·04913 Å^{-1} in devillite) and the intensities of $h00$ reflexions are similar. Furthermore, as in serpierite, the strongest spots have $l = 8n$ on the $h0l$ and $h4l$ layers and $l = 8n + 4$ on the $h2l$ layers, showing that the two minerals have the same prominent pseudo-cell with the same orientation as the true cell, and having $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$ and $c' = \frac{1}{4}c$. From these considerations it follows that the two structures are closely related, notwithstanding the difference in the space groups ($C2/c$ for serpierite, $P2_1/c$ for devillite). Therefore we were led to propose a trial atomic arrangement in devillite derived from the arrangement found in serpierite. In particular the

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *with their standard deviations*

	x	y	z	B
Cu(1)	2469 (5)	4984 (8)	2 (8)	1·90 (7)
Cu(2)	2542 (4)	18 (8)	24 (6)	1·92 (7)
Cu(3)	2560 (3)	7578 (9)	1242 (3)	1·91 (8)
Cu(4)	2591 (3)	2546 (9)	1258 (3)	2·05 (8)
Cu(5)	2500 (3)	5199 (9)	2515 (3)	1·67 (7)
Cu(6)	2500 (3)	211 (9)	2482 (3)	1·80 (7)
Cu(7)	2436 (3)	2538 (9)	3471 (3)	2·05 (8)
Cu(8)	2458 (3)	7592 (9)	3736 (3)	2·06 (9)
Ca(1)	71·(4)	3314 (14)	1502 (4)	1·18 (11)
Ca(2)	5105 (4)	6670 (14)	1506 (4)	1·36 (12)
S(1)	1060 (5)	610 (18)	533 (5)	1·25 (13)
S(2)	957 (5)	302 (19)	2854 (4)	1·17 (12)
S(3)	4031 (5)	4617 (19)	2125 (4)	1·27 (14)
S(4)	3947 (5)	4365 (18)	4463 (5)	1·27 (14)
O(1)	834 (10)	3430 (47)	4909 (10)	1·13 (35)
O(2)	595 (13)	8672 (51)	548 (12)	2·11 (50)
O(3)	896 (12)	2196 (50)	1000 (11)	1·49 (45)
O(4)	1754 (11)	145 (50)	660 (11)	1·80 (42)
O(5)	818 (12)	1802 (50)	2323 (11)	1·69 (46)
O(6)	596 (19)	8447 (75)	2672 (18)	4·77 (80)
O(7)	681 (14)	1160 (58)	3375 (13)	2·72 (55)
O(8)	1672 (12)	9968 (56)	3065 (12)	2·14 (46)
O(9)	4285 (14)	3744 (56)	1624 (14)	2·20 (51)
O(10)	3328 (14)	4906 (55)	1938 (11)	1·94 (44)
O(11)	4126 (18)	2968 (70)	2652 (17)	4·25 (81)
O(12)	4341 (12)	6925 (50)	2267 (11)	1·55 (50)
O(13)	4060 (17)	2721 (67)	3993 (16)	3·86 (75)
O(14)	3232 (12)	4816 (53)	4298 (11)	1·86 (44)
O(15)	4059 (13)	1762 (56)	85 (12)	2·16 (50)
O(16)	4254 (12)	6517 (55)	4461 (11)	2·03 (43)
O(17)	2923 (12)	7416 (50)	494 (11)	1·37 (43)
O(18)	2914 (11)	2505 (42)	522 (10)	1·11 (40)
O(19)	2079 (10)	4898 (50)	873 (10)	1·10 (37)
O(20)	3058 (10)	−23 (50)	1631 (10)	1·37 (38)
O(21)	2132 (10)	7444 (45)	1956 (10)	0·87 (37)
O(22)	2128 (12)	2519 (50)	1959 (12)	1·63 (45)
O(23)	2923 (15)	7667 (58)	3046 (14)	2·71 (58)
O(24)	2889 (11)	2454 (47)	3054 (11)	1·27 (40)
O(25)	1966 (13)	5134 (60)	3353 (13)	2·70 (52)
O(26)	2941 (15)	9898 (67)	4145 (15)	3·32 (63)
O(27)	2030 (12)	7321 (52)	4482 (12)	1·68 (46)
O(28)	2020 (13)	2597 (55)	4500 (13)	2·06 (50)
O(29)	701 (16)	6567 (67)	1610 (15)	0·76 (35)
O(30)	577 (13)	5324 (59)	3773 (13)	2·53 (52)
O(31)	448 (14)	9112 (56)	4530 (13)	2·34 (55)
O(32)	4403 (16)	5932 (65)	441 (15)	3·43 (67)
O(33)	4501 (13)	9931 (60)	1190 (13)	2·66 (54)
O(34)	4213 (10)	8496 (45)	3373 (9)	0·76 (35)

similarity of $h00$ reflexions in the two minerals suggested the existence, in devillite, of copper–oxygen layers parallel to (100) planes analogous to those present in serpierite. Attempts to find the best location of these layers in the cell were verified by comparing observed and calculated structure factors. That giving the best agreement proved to be the correct one and the structure was completed by a Fourier synthesis computed with the signs given by the sheets of copper coordination polyhedra.

The refinement of the structure was begun by means of Fourier difference syntheses, and continued with the least-squares method using a block-diagonal program written by Shiono for the IBM 1130 computer. In the first few cycles of computation we encountered some difficulties: severe oscillations of some parameters occurred and some temperature factors became negative. The R index remained as high as 0·18. Geller (1961) pointed out that, when considerable overlap of crystallographically non-equivalent interatomic vectors in Patterson space occurs, high correlations of pairs of parameters may prevent convergence. This is the case in devillite, and the failure in attaining convergence was ascribed to the high pseudo-symmetry of the structural model, which exhibits a pronounced substructure. The difficulties were overcome by introducing a damping factor for parameter shifts from 0·5 to 0·15. Convergence was attained in four cycles, each followed by a proper rescaling of data. The R index, $\sum ||F_o| - |F_c||/\sum |F_o|$, was 0·11 for all observed reflexions. Data were weighted using the Hughes (1941) scheme. Unobserved reflexions were excluded from the calculations as well as the 200, 400 and 600 reflexions, which were presumably affected by extinction. Final atomic coordinates and isotropic temperature factors are given in Table 1.

A distinction among oxygen atoms, hydroxyl groups and water molecules was made on the basis of Pauling's electrostatic valence rule: the oxygen atoms from O(17) to O(28) belong to OH groups, and those from O(29) to O(34) to H_2O molecules. Observed and calculated structure factors are listed in Table 2. Calculations were performed using the atomic scattering factors given in
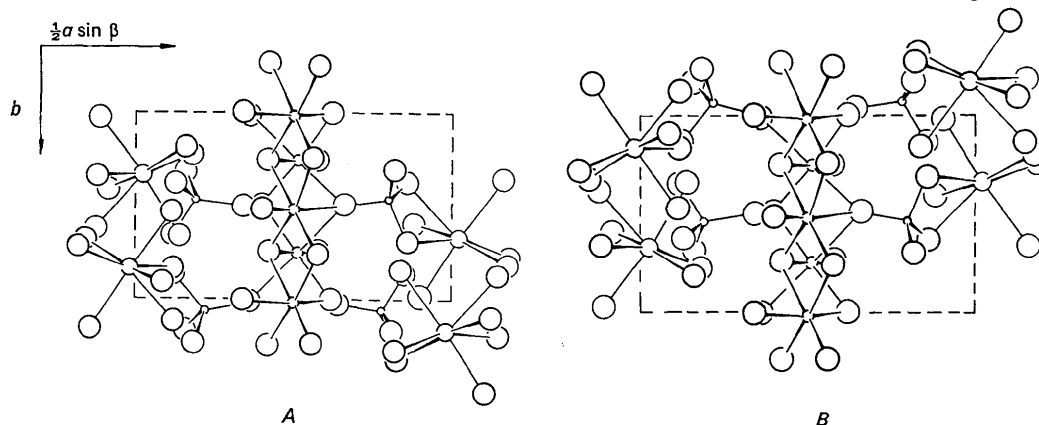

$\frac{1}{2}a \sin \beta$

b

A

B

Fig. 3. *A* and *B* individuals of devillite twin, projected along the c axis.

Table 2. *Observed and calculated structure factors* ($\times 10$)

International Tables for X-ray Crystallography (1962) for Cu, Ca, S and O.

Discussion of the structure

A projection of the devillite structure along the b axis is shown in Fig. 1. Tables 3 and 4 list bond lengths and angles.

All the eight copper ions in the asymmetric unit exhibit the usual $4+2$ coordination, with bond lengths in agreement with the generally accepted ones. The average Cu–O distance in the planar squares formed

Table 3. *Bond lengths*

i	x	y	z	vi	−x	y−½	½−z
ii	x	½−y	z−½	vii	−x	y+½	½−z
iii	x	3/2−y	z−½	viii	1−x	½+y	½−z
iv	x	y−1	z	ix	1−x	y−½	½−z
v	x	1+y	z	x	x	½−y	½+z

Cu(1ⁱ)–O(17ⁱ)	1·96 Å	Cu(2ⁱ)–O(18ⁱ)	1·94 Å
–O(18ⁱ)	2·01	–O(17ⁱᵛ)	1·98
–O(28ⁱⁱ)	2·04	–O(27ⁱⁱ)	2·02
–O(27ⁱⁱⁱ)	2·11	–O(28ⁱⁱ)	2·03
–O(19ⁱ)	2·26	–O(14ⁱⁱ)	2·39
–O(26ⁱⁱⁱ)	2·33	–O(4ⁱ)	2·39

Cu(3ⁱ)–O(20ⁱ)	1·90	Cu(4ⁱ)–O(19ⁱ)	1·88
–O(17ᵛ)	1·97	–O(18ⁱ)	1·90
–O(21ⁱ)	1·98	–O(20ⁱ)	1·94
–O(19ⁱ)	2·00	–O(22ⁱ)	2·00
–O(4ᵛ)	2·45	–O(10ⁱ)	2·39
–O(10ⁱ)	2·56	–O(4ⁱ)	2·44

Cu(5ⁱ)–O(21ⁱ)	1·90	Cu(6ⁱ)–O(22ⁱ)	1·89
–O(23ⁱ)	2·00	–O(24ⁱ)	1·93
–O(22ⁱ)	2·10	–O(23ⁱᵛ)	2·07
–O(24ⁱ)	2·12	–O(21ⁱᵛ)	2·11
–O(25ⁱ)	2·37	–O(8ⁱᵛ)	2·38
–O(10ⁱ)	2·37	–O(20ⁱ)	2·43

Cu(7ⁱ)–O(24ⁱ)	1·96	Cu(8ⁱ)–O(26ⁱ)	1·85
–O(25ⁱ)	1·97	–O(25ⁱ)	1·91
–O(26ⁱᵛ)	2·03	–O(23ⁱ)	1·99
–O(28ⁱ)	2·06	–O(27ⁱ)	2·05
–O(14ⁱ)	2·31	–O(8ⁱ)	2·44
–O(8ⁱᵛ)	2·49	–O(14ⁱ)	2·49

Ca(1ⁱ)–O(30ᵛⁱ)	2·28	Ca(2ⁱ)–O(11ᵛⁱⁱⁱ)	2·32
–O(5ⁱ)	2·31	–O(13ᵛⁱⁱⁱ)	2·35
–O(3ⁱ)	2·35	–O(33ⁱ)	2·39
–O(31ᵛⁱ)	2·36	–O(34ⁱˣ)	2·39
–O(29ⁱ)	2·37	–O(32ⁱ)	2·53
–O(7ᵛⁱⁱ)	2·40	–O(9ⁱ)	2·53
–O(6ᵛⁱ)	2·54	–O(12ⁱ)	2·57

S(1ⁱ)–O(4ⁱ)	1·44	S(2ⁱ)–O(6ⁱᵛ)	1·38
–O(1ⁱⁱ)	1·48	–O(5ⁱ)	1·47
–O(3ⁱ)	1·51	–O(8ⁱᵛ)	1·48
–O(2ⁱᵛ)	1·54	–O(7ⁱ)	1·50

S(3ⁱ)–O(9ⁱ)	1·44	S(4ⁱ)–O(16ⁱ)	1·47
–O(10ⁱ)	1·44	–O(14ⁱ)	1·48
–O(11ⁱⁱ)	1·53	–O(13ⁱ)	1·51
–O(12ⁱ)	1·56	–O(15ˣ)	1·52

Estimated standard deviations for Ca–O, Cu–O and S–O bond lengths are ≤0·04 Å.

Table 4. *Bond angles*

O(17ⁱ)—Cu(1ⁱ)–O(18ⁱ)	99°	O(18ⁱ)—Cu(2ⁱ)–O(17ⁱᵛ)	106°
–O(28ⁱⁱ)	178	–O(27ⁱⁱ)	172
–O(27ⁱⁱⁱ)	79	–O(28ⁱⁱ)	82
–O(19ⁱ)	76	–O(14ⁱⁱ)	97
–O(26ⁱⁱⁱ)	101	–O(4ⁱ)	83
O(18ⁱ)—Cu(1ⁱ)–O(28ⁱⁱ)	80	O(17ⁱ)—Cu(2ⁱ)–O(27ⁱⁱ)	81
–O(27ⁱⁱⁱ)	177	–O(28ⁱⁱ)	171
–O(19ⁱ)	72	–O(14ⁱⁱ)	99
–O(26ⁱⁱⁱ)	105	–O(4ⁱ)	88
O(28ⁱ)—Cu(1ⁱ)–O(27ⁱⁱⁱ)	103	O(27ⁱⁱ)—Cu(2ⁱ)–O(28ⁱⁱ)	91
–O(19ⁱ)	104	–O(14ⁱⁱ)	87
–O(26ⁱⁱⁱ)	79	–O(4ⁱ)	92
O(27ⁱⁱⁱ)–Cu(1ⁱ)–O(19ⁱ)	107	O(28ⁱⁱ)—Cu(2ⁱ)–O(14ⁱⁱ)	85
–O(26ⁱⁱⁱ)	75	–O(4ⁱ)	88
O(19ⁱ)—Cu(1ⁱ)–O(26ⁱⁱⁱ)	176	O(14ⁱⁱ)—Cu(2ⁱ)–O(4ⁱ)	173
O(20ⁱ)—Cu(3ⁱ)–O(17ᵛ)	99	O(19ⁱ)—Cu(4ⁱ)–O(18ⁱ)	84
–O(21ⁱ)	88	–O(20ⁱ)	175
–O(19ⁱ)	176	–O(22ⁱ)	92
–O(4ᵛ)	89	–O(10ⁱ)	93
–O(10ⁱ)	91	–O(4ⁱ)	87
O(17ᵛ)—Cu(3ⁱ)–O(21ⁱ)	173	O(18ⁱ)—Cu(4ⁱ)–O(20ⁱ)	97
–O(19ⁱ)	82	–O(22ⁱ)	172
–O(4ᵛ)	86	=O(10ⁱ)	104
–O(10ⁱ)	100	–O(4ⁱ)	83
O(21ⁱ)—Cu(3ⁱ)–O(19ⁱ)	91	O(20ⁱ)—Cu(4ⁱ)–O(22ⁱ)	87
–O(4ᵛ)	94	–O(10ⁱ)	92
–O(10ⁱ)	80	–O(4ⁱ)	88
O(19ⁱ)—Cu(3ⁱ)–O(4ᵛ)	95	O(22ⁱ)—Cu(4ⁱ)–O(10ⁱ)	82
–O(10ⁱ)	85	–O(4ⁱ)	90
O(4ᵛ)—Cu(3ⁱ)–O(10ⁱ)	174	O(10ⁱ)—Cu(4ⁱ)–O(4ⁱ)	173
O(21ⁱ)—Cu(5ⁱ)–O(23ⁱ)	84	O(22ⁱ)—Cu(6ⁱ)–O(24ⁱ)	86
–O(22ⁱ)	98	–O(23ⁱᵛ)	179
–O(24ⁱ)	174	–O(21ⁱᵛ)	102
–O(25ⁱ)	109	–O(8ⁱᵛ)	96
–O(10ⁱ)	87	–O(20ⁱ)	77
O(23ⁱ)—Cu(5ⁱ)–O(22ⁱ)	176	O(24ⁱ)—Cu(6ⁱ)–O(23ⁱᵛ)	95
–O(24ⁱ)	102	–O(21ⁱᵛ)	172
–O(25ⁱ)	77	–O(8ⁱᵛ)	86
–O(10ⁱ)	96	–O(20ⁱ)	110
O(22ⁱ)—Cu(5ⁱ)–O(24ⁱ)	76	O(23ⁱᵛ)—Cu(6ⁱ)–O(21ⁱᵛ)	77
–O(25ⁱ)	106	–O(8ⁱᵛ)	84
–O(10ⁱ)	81	–O(20ⁱ)	102
O(24ⁱ)—Cu(5ⁱ)–O(25ⁱ)	74	O(21ⁱᵛ)—Cu(6ⁱ)–O(8ⁱᵛ)	92
–O(10ⁱ)	91	–O(20ⁱ)	73
O(25ⁱ)—Cu(5ⁱ)–O(10ⁱ)	161	O(8ⁱᵛ)—Cu(6ⁱ)–O(20ⁱ)	161
O(24ⁱ)—Cu(7ⁱ)–O(25ⁱ)	88	O(26ⁱ)—Cu(8ⁱ)–O(25ⁱ)	177
–O(26ⁱᵛ)	92	–O(23ⁱ)	93
–O(28ⁱ)	176	–O(27ⁱ)	87
–O(14ⁱ)	91	–O(8ⁱ)	94
–O(8ⁱᵛ)	83	–O(14ⁱ)	93
O(25ⁱ)—Cu(7ⁱ)–O(26ⁱᵛ)	179	O(25ⁱ)—Cu(8ⁱ)–O(23ⁱ)	89
–O(28ⁱ)	95	–O(27ⁱ)	90
–O(14ⁱ)	89	–O(8ⁱ)	89
–O(8ⁱᵛ)	93	–O(14ⁱ)	85
O(26ⁱᵛ)–Cu(7ⁱ)–O(28ⁱ)	86	O(23ⁱ)—Cu(8ⁱ)–O(27ⁱ)	175
–O(14ⁱ)	90	–O(8ⁱ)	84
–O(8ⁱᵛ)	88	–O(14ⁱ)	92
O(28ⁱ)—Cu(7ⁱ)–O(14ⁱ)	86	O(27ⁱ)—Cu(8ⁱ)–O(8ⁱ)	101
–O(8ⁱᵛ)	100	–O(14ⁱ)	84
O(14ⁱ)—Cu(7ⁱ)–O(8ⁱᵛ)	173	O(8ⁱ)—Cu(8ⁱ)–O(14ⁱ)	172
O(30ᵛⁱ)–Ca(1ⁱ)–O(5ⁱ)	98	O(11ᵛⁱⁱⁱ)–Ca(2ⁱ)–O(13ᵛⁱⁱⁱ)	80
–O(3ⁱ)	95	–O(33ⁱ)	100
–O(31ᵛⁱ)	78	–O(34ⁱˣ)	84
–O(29ⁱ)	170	–O(32ⁱ)	166
–O(7ᵛⁱⁱ)	105	–O(9ⁱ)	122
–O(6ᵛⁱ)	80	–O(12ⁱ)	82

Table 4 (cont.)

O(5^i)----Ca(1^i)-O(3^i)	80	O(13^{viii})-Ca(2^i)-O(33^i)	92		
-O(31^{vi})	159	-O(34^{ix})	78		
-O(29^i)	90	-O(32^i)	87		
-O(7^{vii})	123	-O(9^i)	146		
-O(6^{vi})	80	-O(12^i)	158		
O(3^i)----Ca(1^i)-O(31^{vi})	80	O(33^i)----Ca(2^i)-O(34^{ix})	168		
-O(29^i)	81	-O(32^i)	74		
-O(7^{vii})	146	-O(9^i)	107		
-O(6^{vi})	158	-O(12^i)	77		
O(31^{vi})-Ca(1^i)-O(29^i)	93	O(34^{ix})----Ca(2^i)-O(32^i)	100		
-O(7^{vii})	78	-O(9^i)	79		
-O(6^{vi})	119	-O(12^i)	115		
O(29^i)----Ca(1^i)-O(7^{vii})	75	O(32^i)----Ca(2^i)-O(9^i)	73		
-O(6^{vi})	106	-O(12^i)	108		
O(7^{vii})--Ca(1^i)-O(6^{vi})	54	O(9^i)----Ca(2^i)-O(12^i)	56		
O(4^i)----S(1^i)----O(1^{ii})	111	O(6^{iv})----S(2^i)--O(5^i)	106		
-O(3^i)	111	-O(8^{iv})	115		
-O(2^{iv})	117	-O(7^i)	104		
O(1^{ii})--S(1^i)--O(3^i)	108	O(5^i)----S(2^i)--O(8^{iv})	110		
-O(2^{iv})	105	-O(7^i)	111		
O(3^i)--S(1^i)--O(2^{iv})	104	O(8^{iv})----S(2^i)--O(7^i)	110		
O(9^i)--S(3^i)--O(10^i)	110	O(16^i)----S(4^i)--O(14^i)	104		
-O(11^i)	110	-O(13^i)	118		
-O(12^i)	107	-O(15^{ix})	116		
O(10^i)--S(3^i)--O(11^i)	105	O(14^i)----S(4^i)--O(13^i)	105		
-O(12^i)	107	-O(15^{ix})	105		
O(11^i)--S(3^i)--O(12^i)	118	O(13^i)----S(4^i)--O(15^{ix})	108		

Estimated standard deviations for O-Cu-O and O-Ca-O angles are ≤1° and for O-S-O angles are ≤2°.

by the four nearest oxygen atoms of each tetragonal bipyramid is 1·99 Å, while the average value for the two longer Cu-O distances in these polyhedra is 2·41 Å. The configuration of copper-oxygen complexes is as follows:

Cu(1) binds 4(OH) and 2O
Cu(2) binds 4(OH) and 2O
Cu(3) binds 5(OH) and 1O
Cu(4) binds 5(OH) and 1O
Cu(5) binds 5(OH) and 1O
Cu(6) binds 5(OH) and 1O
Cu(7) binds 4(OH) and 2O
Cu(8) binds 4(OH) and 2O.

Each copper polyhedron shares six edges with six adjacent copper polyhedra, giving rise to a distorted hexagonal close packing of copper and oxygen atoms. The Cu-Cu distances between neighbouring ions range from 3·04 to 3·27 Å. The resulting sheets, one of which is shown in Fig. 2 projected along the a axis, run parallel to (100) planes at $x=\frac{1}{4}$ and $\frac{3}{4}$; within the sheet the repetition unit is $^2_\infty[Cu_2(OH)_3O]^-$. This arrangement of copper-oxygen complexes can be regarded as derived from a hypothetical $Cu(OH)_2$ structure of the $C6$ type, in which one quarter of hydroxyl groups are replaced by oxygen atoms of SO_4^{2-} groups. These complex layers are closely similar to those found in serpierite; the crystal structures of these minerals are the only known structures where such an arrangement of copper-oxygen polyhedra is present.

Ca ions are in sevenfold coordination and bind four oxygen atoms and three water molecules with distances in the range 2·28 to 2·57 Å; the average values of the
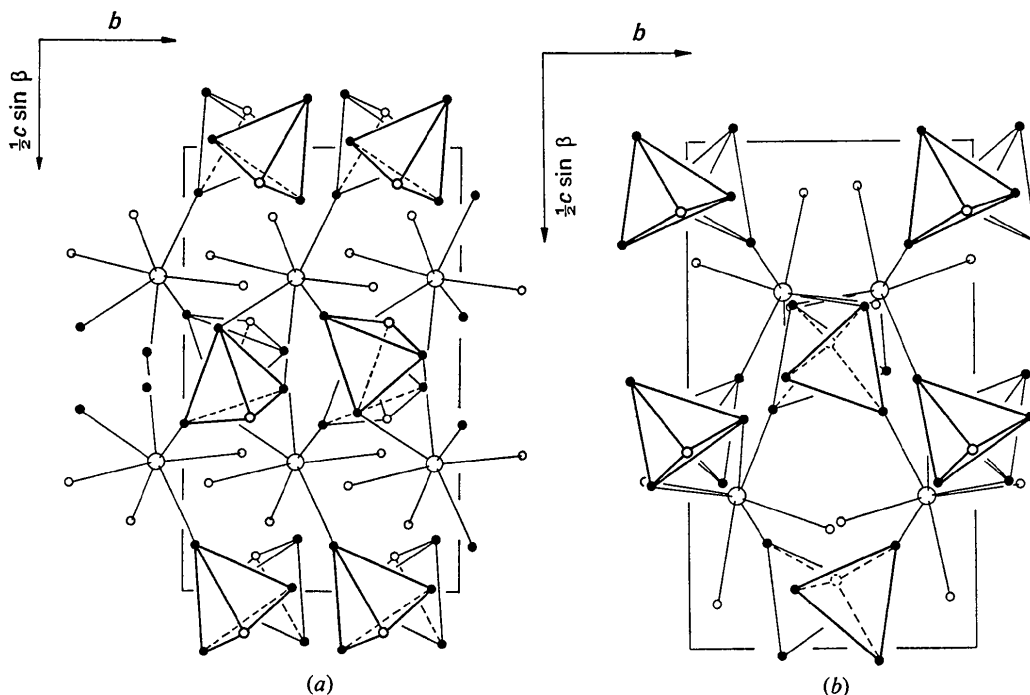

Fig. 4. The arrangement of Ca polyhedra and SO_4^{2-} tetrahedra, projected along [100] (a) in serpierite and (b) in devillite. In the SO_4^{2-} tetrahedra open circles are oxygen atoms linked to Cu ions; in the Ca polyhedra open circles are water molecules.

Ca–O distances for the two crystallographically non-equivalent ions are 2·37 and 2·44 Å.

The SO_4^{2-} groups are nearly tetrahedral, the mean value of S–O bond lengths being 1·48 Å. Each of these tetrahedra is linked to a copper–oxygen layer by a vertex; both S(3) and S(4) share a vertex and an edge with two adjacent Ca polyhedra. S(1) and S(2) are each linked through a corner to one calcium ion and have two oxygen atoms unshared by cations.

Several contacts between oxygen atoms not belonging to the same coordination polyhedron are listed in Table 5. They may represent hydrogen bonds, and are in the range from 2·61 to 2·99 Å; two longer distances between O(3) and O(19) (3·04 Å) and between O(5) and O(22) (3·05 Å) are probably very weak bridges.

Table 5. *Hydrogen bonds*

O(1^i)—O(28^i)	2·86 Å
O(1^i)—O(30^i)	2·72
O(1^i)—O(31^{iv})	2·84
O(2^i)—O(31^{iii})	2·79
O(2^i)—O(29^i)	2·65
O(3^i)—O(22^i)	2·96
O(6^i)—O(29^i)	2·67
O(7^i)—O(30^i)	2·73
O(9^i)—O(33^{iv})	2·61
O(11^i)–O(24^i)	2·93
O(12^i)–O(34^i)	2·70
O(13^i)–O(24^i)	2·84
O(13^i)–O(26^{iv})	2·99
O(15^i)–O(18^i)	2·81
O(15^i)–O(32^i)	2·73
O(16^i)–O(34^i)	2·69
O(16^i)–O(32^{iii})	2·64
O(21^i)–O(29^i)	2·96
O(23^i)–O(34^i)	2·68
O(3^i)—O(19^i)	3·04
O(5^i)—O(22^i)	3·05

The structure of devillite can be schematically described as built up from copper–oxygen layers parallel to (100) bound together by complex sheets formed by SO_4^{2-} and Ca–O polyhedra. This sheet-like feature in the structure accounts for some physical properties of the mineral, such as the perfect cleavage {100} and the negative optical character.

Twinning in devillite

Devillite crystals are twinned according to two different laws. The first type of twinning is a twinning by pseudomerohedry, with reflexion plane (100). This twinning is responsible for the splitting of spots on the photographs and has been described above.

The second type of twinning is not considered in Friedel's (1926) classification, and is the cause of the spread in reflexions having $k+l$ odd. As in serpierite, copper ions and oxygens atoms of the copper coordination polyhedra have particular locations: they contribute almost entirely to the structure factors with

$k+l$ even. Since these reflexions are not diffuse, it can be concluded that the stacking of copper–oxygen layers does not change in the whole crystal. The multiple break in periodicity, which causes the spreading-out of spots, is to be ascribed to a rearrangement of sulphur and calcium layers alternating with the copper–oxygen sheets, and must be such as to affect only the reflexions with $k+l$ odd. Considering the trigonometric parts of the F_c formulae in $P2_1/c$ space group, we have:

$$A = 4 \cos 2\pi(hx+lz) \cos 2\pi ky \text{ for } k+l=2n$$
$$A = -4 \sin 2\pi(hx+lz) \sin 2\pi ky \text{ for } k+l=2n+1$$

The condition required is attained if the y coordinate of an atom of the A individual is changed to $-y$ for the same atom in the B individual. In fact we have $\cos 2\pi ky = \cos 2\pi k(-y)$ for the sharp reflexions, and $\sin 2\pi ky = -\sin 2\pi k(-y)$ for the diffuse reflexions, i.e. from one individual to the other in a twin there is a lack of periodicity affecting these reflexions. The spread of reflexions take place along the a^* reciprocal axis, i.e. a discontinuity occurs through the copper–oxygen layers which remain virtually unchanged, and which represent the slice of structure which bridges both individuals of the twin. A and B individuals, projected along the c axis, are shown in Fig. 3. The twin operations at the boundary between two individuals are twofold screw-axes parallel to [010] at $\frac{1}{4}a$ and $\frac{1}{4}c$, and crystallographically related positions, and inversion centres at $\frac{1}{4},0,0$; $\frac{1}{4},\frac{1}{2},0$ etc. These pseudosymmetry operations pre-exist in the copper–oxygen layers which have the symmetry necessary for twinning, according to Holser's (1958) theory. This type of twinning, very similar to that found in serpierite, is not given in Friedel's geometrical classification, since the point symmetry of the twinned crystal is the same as that of a single individual. Twins of this kind cannot be distinguished from single crystals by a morphological study.

Relationships between devillite and serpierite

As expected from the close analogies in chemical constitution, in physical properties, in twinning laws, and from the striking similarities of diffraction patterns of devillite and serpierite, the packing of the atoms is very similar in the two minerals, despite the difference in space groups. Both structures have layers in which copper–oxygen complexes are packed in an essentially identical way. Differences occur in bond distances within a single coordination polyhedron; in devillite all Cu ions have 4+2 coordination; in serpierite only three of the five independent ions have this configuration. Of the other two ions, one has a nearly regular octahedral coordination, and the other has a configuration intermediate between the octahedral and the bipyramidal coordination. The first should probably be considered entirely as a Zn ion, while the second polyhedron would be due to a partial substitution of zinc

by copper. This arrangement of Cu and Zn ions in the structure is in agreement with the results of chemical analysis (Cu:Zn atomic ratio of 1·9) and serpierite can be regarded as a mineral of calcium, copper and zinc having the formula:

$$Ca_2Cu_5Zn(Zn_{0.88}Cu_{0.12})_2(OH)_{12}(SO_4)_4 \cdot 6H_2O$$
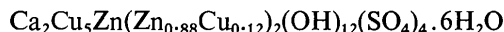
The chief difference between devillite and serpierite is in the reciprocal stacking of copper–oxygen layers; in devillite two adjacent layers are shifted by $\frac{1}{4}b$ with respect to the array they have in serpierite: this fact causes a rearrangement of the calcium–oxygen polyhedra and SO_4^{2-} groups, which form the layers interposed between the copper–oxygen sheets. In Fig. 4 S and Ca layers in the two minerals are schematically shown. It is interesting to note that, notwithstanding the rearrangement of the atoms, the configuration of each Ca ion in devillite, and the role played in the structure, are the same as in serpierite.

References

Březina, A. (1879). Z. Kristallogr. 3, 357.
Faraone, D., Sabelli, C. & Zanazzi, P. F. (1967). Rend. Accad. Naz. Lincei, 43, 369.
Friedel, G. (1926). Leçons de Cristallographie. Paris: Berger–Levrault.
Geller, S. (1961). Acta Cryst. 14, 1026.
Grainger, C. T. (1969). Acta Cryst. A25, 427.
Holser, W. T. (1958). Z. Kristallogr. 110, 249.
Hughes, E. W. (1941). J. Amer. Chem. Soc. 63, 1737.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
Meixner, H. (1940). Zbl. Miner. Geol. Paläont. A,p. 244.
Palache, C., Berman, H. & Frondel, C. (1951). The System of Mineralogy, Vol. II, p. 590. New York: John Wiley.
Pisani, F. (1864). C. R. Acad. Sci. Paris, 59, 813.
Sabelli, C. & Zanazzi, P. F. (1968). Acta Cryst. B24, 1214.
Szabo, J. (1879). Tschermaks. Mineralog. Petrog. Mitt. 2, 311.
Wappler, G. (1965). Z. Kristallogr. 121, 467.

The Crystal and Molecular Structure of cis-4-t-Butylcyclohexane-1-carboxylic Acid

By H. van Koningsveld

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, Delft, The Netherlands

The structure of cis-4-t-butylcyclohexane-1-carboxylic acid, $C_{11}O_2H_{20}$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit cell, of dimensions $a = 17\cdot132$, $b = 6\cdot271$, $c = 10\cdot380$ Å and $\beta = 92\cdot17°$, contains four molecules. The structure has been solved using a symbolic phasing procedure and Fourier synthesis. Refinement by the least-squares (block-diagonal approximation) method converged to a final R index of 5·7% for 1542 independent non-zero reflexions. The structure consists of infinite zigzag chains of molecules along the a axis. In each chain the antipodes form centric dimers through approximately linear hydrogen bonds of 2·640 Å. The axial carboxyl group is nearly coplanar with an α,β-bond in the ring (torsion angle $= 6\cdot4°$), the carbonyl oxygen being eclipsed with the C^β atom. The equatorial t-butyl group is twisted away by about 8° from the prefectly staggered form and a puckering of the t-butyl side of the ring is observed; the mean C–C–C bond angle, mean C–C bond distance and mean torsion angle in the ring are 111·5°, 1·529 Å and 54·8° respectively.

Introduction

X-ray studies on carboxylic acids (Groth & Hassel, 1965; Dunitz & Strickler, 1966; Kanters, Kroon, Peerdeman & Schoone, 1967), pK_a-measurements on cyclohexanecarboxylic acids (Sicher, Tichý & Šipoš, 1966; van Bekkum, Verkade & Wepster, 1971), empirical valence force-field calculations (Altona & Sundaralingam, 1970) and nuclear magnetic resonance spectroscopic studies on t-butylcyclohexane (Remijnse, van Bekkum & Wepster, 1971) show some interesting features:

1. The carbonyl oxygen atom (in an axial carboxyl group if cyclohexanecarboxylic acids are considered) is always in an (almost) eclipsed position with the α-substituent or β-carbon atom; however, a few exceptions have been found (Bootsma & Schoone, 1967; Kadoya, Hanazaki & Iitaka, 1965);

2. The generally accepted perfectly staggered conformation of t-butylcyclohexane is not confirmed by valence force calculations: the t-butyl group should be twisted away by $\pm 17°$;

3. The calculated bond angles, bond distances and torsion angles in the cyclohexane ring have anomalous values at the t-butyl side of the ring.

The aim of this investigation was to verify these aspects by determining the molecular structure of cis-4-t-butylcyclohexane-1-carboxylic acid (CIS):