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 $1\cdot 11$ Å. The distance between two oxygen atoms of adjacent methoxyl groups is $2\cdot 653$ Å. The shortest intermolecular contacts are listed in Table 9.

The authors thank Professors G. Adembri, F. De Sio, R. Nesi and M. Scotton of the Istituto de Chimica Organica of Florence University for providing the crystals and for very useful discussions, and the Consiglio Nazionale delle Ricerche, Roma for the financial assistance.

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.

Acta Cryst. (1972). B28, 1182

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

(Received 1 October 1971)

Devillite, $CaCu_4(OH)_6(SO_4)_2$. $3H_2O$, is monoclinic, space group $P2_1/c$; with a=20.870, b=6.135, c=22.191 Å, $\beta=102^{\circ}44'$ 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 $c_{co}^{2}[Cu_{2}(OH)_{3}O]^{-}$ 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 bluishgreen plates flattened on {001} and striated along [010]. The lattice parameters are a = 20.870 (2), b =6.135 (2), c = 22.191 (3) Å, $\beta = 102^{\circ}44$ (1)', as determined in a previous paper (Faraone, Sabelli & Zanazzi,

^{*} Paper presented at the V Congress of the Italian Crystallographic Association, Bari, October 1971.

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 α 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 $180^\circ-2\beta^*$, *i.e.* $25^\circ28'$. According to Friedel's (1926) geometrical notation, devillite is twinned by pseudomerohedry, 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 hk0and hk24 reflexions from the A individual overlap the $h\bar{k}0$ 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 $\alpha_1-\alpha_2$ 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 (×10⁴) and isotropic temperature factors (Å²) with their standard deviations

	x	v	z	В
Cu(1)	2469 (5)	4984 (8)	2 (8)	1.90 (7)
Cu(2)	2542(4)	18 (8)	24(6)	1.92(7)
$\tilde{C}u(3)$	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)	2.05(0)
Ca(1)	$71 \cdot (4)$	3314(14)	1502(4)	1.18(11)
Ca(2)	5105 (4)	6670 (14)	1506 (4)	$1 \cdot 36(12)$
S(1)	1060 (5)	610 (18)	533 (5)	1.25(12)
S(2)	957 (5)	302(19)	2854 (4)	$1 \cdot 17 (12)$
S(3)	4031 (5)	4617(19)	2125(4)	1.27(12)
S(4)	3947 (5)	4365 (18)	4463 (5)	1.27(14) 1.27(14)
Õ	834 (10)	3430 (47)	4909 (10)	$1 \cdot 13 (35)$
O(2)	595 (13)	8672 (51)	548 (12)	2.11(50)
$\tilde{O}(3)$	896 (12)	2196(50)	1000 (11)	1.49(45)
O (4)	1754 (11)	145(50)	660 (11)	1.80(42)
ŌĠ	818 (12)	1802 (50)	2323 (11)	1.69(42)
ŌĞ	596 (19)	8447 (75)	2672 (18)	4.77 (80)
$\tilde{O}(\tilde{7})$	681 (14)	1160 (58)	3375 (13)	2.72(55)
0(8)	1672(12)	9968 (56)	3065 (12)	2.12(33) 2.14(46)
0(9)	4285 (14)	3744 (56)	1624(14)	2.14(40) 2.20(51)
O(10)	3328(14)	4906 (55)	1938 (11)	1.94(44)
o(iii)	4126 (18)	2968 (70)	2652 (17)	4.25 (81)
O(12)	4341 (12)	6925 (50)	2052(11)	1.55(01)
O(13)	4060 (17)	2721 (67)	3993 (16)	3.86 (75)
O(14)	3232 (12)	4816 (53)	4798 (11)	1.86(13)
0(15)	4059 (13)	1762 (56)	85 (12)	2.16(50)
0(16)	4254 (12)	6517 (55)	4461(11)	2.03(30)
O(17)	2923 (12)	7416 (50)	401 (11)	1.37(43)
O(18)	2914(11)	2505(42)	522 (10)	1.11(40)
O(19)	2079 (10)	4808 (50)	972 (10) 872 (10)	1.10(40)
O(20)	3058 (10)	-23(50)	1631 (10)	1.27(28)
O(21)	2132 (10)	7444 (45)	1051 (10)	0.87(30)
O(22)	2132(10) 2128(12)	2519 (50)	1950 (10)	1.63(45)
O(23)	2923(15)	7667 (58)	3046 (14)	2.71(58)
O(24)	2889 (11)	2454 (47)	3054 (11)	1.27(30)
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)
$O(\overline{28})$	2020(12)	2597 (55)	4500 (13)	2.06(50)
O(29)	701 (16)	6567 (67)	1610 (15)	0.76(35)
Q(30)	577 (13)	5324 (59)	3773 (13)	2.53 (52)
0(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 Rindex, $\sum ||F_o| - |F_c|| / \sum |F_o|$, 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 H₂O molecules. Observed and calculated structure factors are listed in Table 2. Calculations were performed using the atomic scattering factors given in



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

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

×. 0. 0 8 2040 3834	H. 0. 16 0 4202 3896	-3 793 -860 7 1293 1485 9 548 629	H. 1. 14 1. 529 -471	-10 451 1003 12 553 655 -12 1319-1521	-2 8207-7604 4 4878 4519 -4 7652 7055	-1 +02 +72	-7 768 -643 -9 420 -646 11 702 Alb	-2 217 280 -6 65 642 -0 686 -756	-4 418 576 -0 967 -004 8 740 -000
10 1823-2366 14 5378 5810 14 3152-3276 16 3011 3084 18 2330-2256	2 4857-4657 -2 5784-5877 - 4 2851 2711 6 4912-4847	-13 003 -079 -13 003 -079 15 715 /52 -15 381 -107 1/ 642 377	-3 379 370 5 799 -753 -5 457 348 13 647 -717	10 1514 1571 -16 1015-1018 -18 1478 1434 20 445 444	-0 +302-+328 8 2+42 2+43 -8 +423 +254 10 2548-3076	H, 2, 26 0 443 -502 2 458 -442	17 648 633 19 321 303 Ma 34 23	-10 245 -218 -12 108 183 H. 3, 20	10 003 041 -10 088 -350 -12 807 1035 14 900 108 -14 339 -410
20 3673 3245 22 2203-1936 24 2026 1576 26 2001-1673	-6 2216-2260 6 1920 2134 -8 4215 4170 10 3003-3604 -10 3875-3770	14 623 543 -14 756 704 23 641 525 -23 405 246	H. L. 15 2 10/1 408 2 246 255	22 ROV -702 -22 EVE 57 24 886 848 -24 ELEO-1726	12 1196 1817 -12 2160 2610 16 1755-1929 -14 1766-2052	-8 857 -855 H. J. Q	0 436 -851 2 431 -500 -2 720 146 4 170 -865	-1 263 - 554 H. A. O 2 4921-6756	16 717 -782 +16 655 668 18 733 639 -18 114 -104 -20 675 793
0 507 -609 2 677 -702 -7 371 -405	-12 2002 2086 1+ 1811-1645 -14 4156-4541 15 1344 855	0 1732-1666 2 3755-3677 -2 1652 1543	-0 443 -414 -8 623 -500 -10 479 -447 -12 417 -415	H, 2, 3 -1 1018 -989 -3 1470-1511	-16 3077 3529 18 2261-2071 -18 2655-2275 20 1297 1290	5 +21 516 7 +46 11 +72 -411 13 8+5 -808 21 +99 -488	-6 509 -537 -8 1171-1167 10 225 306 -10 443 -491 -12 356 -294	4 3715 4364 6 1338-3438 8 3019 1158 10 2465-2380 12 2285 2217	-22 547 -485 H. 4. 11 1 560 501
-+ 256 572 6 11 54 1-12 -6 1024-1308 10 3-1 405	-10 2024 321 -16 1231-1244 -16 1420-1385 -20 2373 2214 -22 2247-2030	-4 2190 2575 -6 381 787 8 680 815 10 305 322	-14 297 516 18 493 -54 -20 890 -859	11 000 -091 -11 753 -817 -13 1103-1159 -15 500 -510	-22 1873-1837 -24 1972 1822 	H. J. 1 2 442 319 3 540 895	16 213 -176 -16 106 -151 18 264 251 -18 1014 -185 -20 623 -595	14 2417-2487 16 1502 1404 18 1431-1837 20 1853 1417 22 1272-1278	3 622 553 5 579 606 -5 810 -647 7 604 -14 -7 926 -750
12 2672-2984 12 1024 1124 14 599 -298	H, 0, 18	12 1444-1524 -12 219 251 14 470 354 -14 782 664	-3 543 554 5 521 -482 -5 1188 484	-23 648 -802 -25 307 -371 	3 736 -645 -1 516 475 5 551 -487 -3 545 520 -3 545 520	-4 347 366 6 1284 1484 -6 577 583 13 208 -742 -10 283 189	-24 351 -327 He 34 12	H, 4, 1 1 1421-1151 -1 1028 806	9 340 460 11 454 552 -17 557 -553 -21 328 380
16 1781 1740 16 754 864 18 436 -451 20 1530-1508	-2 1064 847 4 1167 -463 -4 1465-1297 5 516 -550	18 345 -290 -18 572 -502 20 440 -436 22 1007 -834	-13 637 613 -15 665 716 -17 607 665	0 68/0 66/6 2 9131-8843 -2 2943-3141 4 8102 8256	11 645 746 -13 817 817 15 447 -440 -15 806 874	12 726 -746 -12 1026 1054 14 1055-1089 -14 990 964	3 274 104 -3 820 858 5 504 -478 7 832 -623 -7 1004 -865	3 469 -566 9 855 -v28 11 975-1115 13 315 -347 19 748 -823	H. 4.12 0 744 -812 2 636 -517 -6 834 893
22 428 511 -22 1091 -930 24 1442-1256 -24 1016 817	8 611 -579 10 1362 1355 -10 566 -615 12 559 -678	-24 584 488 -26 281 237 Hi Li 6	0 1770 1734 2 724 744 -2 411 -268	0 0177-7093 -0 4287-5797 8 5837 5185 -8 5300 5302	-23 356 485	-16 559 474 18 373 408 -18 456 418 -20 375 294 -22 105 112	-4 804 -706 11 421 503 -11 317 386 13 305 335 -13 899 1027	21 678 -774 H. 4. 2 0 902 -200	8 680 751 -8 745 -707 10 628 -722 14 421 -406 -14 277 -336
H. 0, 4	-14 375 380 -14 336-1333 16 365 -143 -18 1378-1309 -20 600 508	1 400 428 3 587 556 -5 481 -577 -5 411 -485 -7 1191-1451	-4 (405-(315 6 635 -711 8 335 -436 -8 1223 1103 10 708 805	-10 3-07	-2 857 -746 + 1084 -928 -4 182 -575 553 -616 -6 569 -532	-24 359 340 H. 3, 2 3 520 585	-15 357 404 -17 403 -387 -19 714 -607 H, 3, 13	2 544 1/7 -2 589 -603 - 360 345 -4 526 635 -4 526 635 6 900 440	-10 1071 1101 -18 079 -573 -20 416 331 H, 4, 13
+ 2715-27+5 -+ 803 -736 -6 5983-6311 -8 602 -587 10 1288 1316	-22 1045 -881 -24 231 -124 H, 0, 20	-9 888 -952 11 576 552 -11 551 -829 -15 510 -545 17 515 -573	-10 863 737 12 445 423 -12 355 383 -14 491 -536 16 300 -313	16 2324 2333 -16 3156 3225 18 1282-1354 -18 3291-3296 20 1460 1444	8 1153-1150 -8 845 722 10 998 1161 -14 1290-1323 16 998-1062	-3 267 137 -5 759 408 -7 429 541 4 389 -375 -11 754 -792	0 931 879 2 1017 982 -2 312 -296 4 369 390	0 401 -257 -8 331 490 10 595 539 -10 682 -784 12 613 -579	1 1194 1103 -1 804 -655 3 366 361 -3 791 683
-10 1684-1950 12 899 -723 -12 1117 1187 14 1465-1350	0 1867 1573 2 826 575 4 420 419 -4 375 372 -8 1068 1508	-10 780 -662 -21 548 -486 -23 562 -577 H. 1. 7	-18 745 771 -22 419 -328 -24 208 -212 H. 1.18	-20 1095 2950 22 1503-1138 -22 1358-1239 24 687 768 -24 1388 1494	18 642 540 -18 1004 -986 -20 855 947 -22 936 -886 -24 784 648	-13 510 -555 L5 467 480 -17 486 488 23 293 358	-* 915 101* -* 926 1018 * 820 686 -* 749 787 12 1190 128*	14 995 987 -14 005 -684 -16 894 1023 18 813 739 -18 847 -897	5 614 -562 -5 1072 907 7 450 -557 -9 1212-1198 11 319 360
16 949 866 -16 2128-2033 -18 978 -819 20 903 721 22 862 -805	10 771 827 -10 1251 1023 12 487 543 14 251 163 -16 595 -417	0 158 121 2 1493-1533 -2 552 572 4 881 -452	1 401 372 -1 572 -499 -3 694 -383 5 764 721	H. 2. 5 -3 285 -246 5 1109-1140	H. 2. 15 1 596 463	H, 3, 3 0 1872-1642 2 948 -487 -2 1618-1456	14 401 407 16 514 408 -16 733 838 -18 579 593 -22 448 -454	20 547 -700 -20 531 462 22 698 759 -22 1015-1089	-11 880 -487 15 420 -522 -19 697 -749 -21 413 -453
24 358 352 -26 (494-13(3 Mg 0, 6	-18 934 810 -20 1260 1065 -22 718 -596 H, 0, 22	-4 249 148 5 515 -541 -5 328 -440 8 787 -838 -8 602 -712	7 885 721 9 830 844 -9 835 -504 -11 828 -528 -13 722 -585	-5 471 348 7 1650-1871 -7 1648 1746 9 1464-1715 -7 1870 2183	3 661 553 5 655 626 7 662 689 -7 973 -737 9 498 639	4 [147-1259 -4 [402-1370 6 185 91 -6 319 -523 8 326 -304	H, 3, 14 1 501 437 -1 1219-1052	H, 4, 3 1 943 -870 -1 464 -275 3 738 -642	2 680 -639 -2 337 172 -4 432 -310
0 525 375 2 1071 873 -2 700 609 6 2127 2046 -6 875 694	2 1176-1111 -2 #85 747 = 003 -593 -4 548 491	12 379 -386 -12 678 -737 -16 1452-1552 -18 555 -611 -20 867 782	H, L, 19 2 443 - 581 -2 255 -235	11 665 -710 -11 266 1456 -15 686 -617 19 615 -598 -19 441 453	-v 1246-1065 -11 801 -791 -1v 486 -343 H. 2. 18	-8 495 543 10 292 -304 -10 383 -409 12 462 -497 14 877-1032	5 743 -585 -3 544 -417 5 674 -643 -5 556 489 -7 742 621	-3 945 -794 -7 746 809 -9 834 1044 -11 315 448 -15 349 415	6 639 -721 -8 696 -360 12 386 637 -12 671 -612 14 649 -637
6 615 673 -5 1761 1716 8 1501 1571 -8 649 -678 10 938 -980	6 440 -425 8 777 811 -8 1245-1064 10 632 -554 -10 772 716	-22 306 300 -26 593 -538 H. 1. 8		H. 2. 0	2 1211 1056 -2 +30 361 6 +04 375 -6 567 397	-14 972 -995 16 757 -825 -16 836 -877 18 432 -384 -18 612 675	9 519 598 15 395 - 349 17 227 323 H, 3, 15	-17 833 811 -19 525 523	-16 753 -817 -18 404 388 -20 469 -494 H, 4, 15
-10 1461 1641 12 2008 2040 -12 901-1056 14 662 531 -14 1441 1505	12 485 -545 -14 1039 978 -16 772 -775 -18 450 426	-1 604 -344 3 1259-1213 5 1804-1967 -5 1253 1254 7 1530-1652	-12 375 -306 14 274 -243 -18 485 359 -22 251 -223	4 1424-1159 -6 634 -685 8 1476-1616 -8 574 560	-8 1072 884 -10 1104-1200 12 873 907 -12 443 465 14 359 -244	20 245 -184 H. 3. 4 1 1317-1476	0 510 -512 2 372 -391 -2 305 246 4 823 -844	2 551 -183 -2 667 659 4 349 -115 -4 518 336	1 728 -614 -1 390 290 3 755 -751 -3 419 275
-16 1227-1297 18 1070 -979 -18 1404 1261 -20 1092-1026	0 2000 2005 2 2556-2139 -2 2817-2555 6 1706 1601	9 474 -606 -9 1475 1519 15 504 -496 -15 603 -588	H, L, 20 -1 717 -616 -3 669 -336 5 351 -636	-10 1244-1341 12 1184-1237 -12 1040 1290 14 1377 1417 -14 1625-1690	-14 339 -822 16 555 574 -16 646 792 -18 716 591 -20 752 -548	-3 505 -557 5 766 #52 -5 704 -862 7 608 773	6 232 236 -6 419 384 -8 240 224 12 482 -514	-8 615 -441 -8 989 938 10 707 750 -12 1234 1133 14 622 -558	-5 531 400 -9 424 461 -11 510 490 13 319 -435 -13 457 508
-22 691 732 24 1252 1100 -24 1382-1094 -26 345 411	-4 2578 2139 6 1781-1738 -6 3853-3348 8 1163 997 -8 2268 2011	14 509 -548 -19 504 495 -21 790 654	-5 410 208 -7 788 642 -11 613 -539 -13 859 -822 -21 409 -414	16 917 -670 -16 1076 1094 -18 1023 -954 20 1223-1214 -20 1138 1024	H, 2, 17	11 597 -644 -13 593 -559 15 160 345 -15 643 -641 -17 175 416	-14 459 519 16 444 -416 -18 376 391 -22 649 556	-14 675 629 16 539 489 18 502 -245 20 531 568	H, 4, 16 0 3187 2961 2 2823-2703
H. 0, 8 0 3466 4330 2 3732-4633 -2 4349-5057	-10 2358-2301 -12 1931 1514 -14 2189-2269 -16 811 714 -18 1508-1655	0 708 -716 2 1481 1486 -2 418 240 4 1372 1273	H, 1, 21 0 282 361 -2 543 526	-22 480 -443 -24 432 358 H, 2, 7	-5 372 -257 5 871 -797 -5 801 734 -7 948 770 -11 1015 -930	19 389 -362 -19 434 516 -23 401 -484 He 3e 5	H, 3, 20 1 372 207 -1 499 -358 -3 244 162	H, 4, 5 1 587 502 -1 556 478 3 1763 1579	-2 2682-2561 + 3289 3287 -4 2660 2538 6 2139-2237 -6 1799-1558
4 4239 4937 -4 8315 9433 6 4191-4707 -6 7820-8614 8 4634 5382	x, 0, 26 4 335 315 -4 983 1032	-6 1436 1434 -6 472 402 8 314 278 -8 599 -540 10 1196-1521	4 519 -561 -4 751 -691 6 810 -833 -6 1437-1441 8 603 570	1 376 366 3 700 651 -3 429 -416 5 669 623 7 568 641	13 467 -528 -13 690 -742 15 374 -430 -21 388 -402 -23 249 -314	0 569 -559 2 705 -611 -2 179 -260 4 1613 1605	-5 718 490 -9 591 -478 -11 316 -245 13 390 -476 -15 609 606	-3 505 -344 5 1467 1413 -5 1487-1255 -7 1208-1130 9 439 -567	8 2121 2203 -8 2044 2019 10 2009-1907 -10 2399-2427 12 1690 1585
-8 7196 8223 10 0206-5065 -10 5533-6560 12 3260 3960 -12 0971 6696	-10 623 -670 -12 516 391 -14 338 622 -16 635 569	-10 950-1012 12 525 551 -12 286 -287 14 1311 1444 -14 301 340	-6 286 226 10 325 408 -10 516 422 -12 609 547 -14 575 -543	11 392 408 -11 342 498 -19 608 680 21 508 612	H, 2, 18 0 691 504 2 476 -435	6 506 601 -6 524 -407 8 254 343 -8 493 -485 -10 226 -329	-19 281 -355 -21 408 -341 H, 3, 17	-0 377 -405 13 724 853 15 661 840 -15 486 -542	-12 2107 2058 14 653 -688 -14 1896-2032 -16 2337 2317 -18 1653-1394
-14 2200-2752 16 3167 3354 -16 3061 3510 18 3037-2855	N, 0, 20 0 493 -565 -2 179 61 -6 276 202	-16 729 835 -18 486 -425 20 606 -451 -20 596 -105	-18 534 -513 -20 537 504 H, 1, 22	H, 2, 8 0 778 -603 2 1998-1758	-2 770 651 6 612 -499 8 809 851 -10 950 802 14 1176-1156	12 V35 -V65 -12 267 -269 14 958 955 -14 338 171 16 1272 1154	-2 527 -551 -4 883 -939 6 674 -815 -6 903 -162 8 677 -513	0 100V -664 2 414 -483 -7 1017 -943	H, 4, 17
20 1340 1155 -20 2533 2494 22 1702-1501 -24 2580 2147 -26 891 -893	H, 1, 0 3 746-1059 5 358 334	H, 1, 10 1 923 -842 -1 418 355 3 973 -935	1 740 -658 -1 630 517 -7 584 517 9 416 -404 -9 828 747	4 1008 839 -4 2175 1993 6 648 610 -5 1082-1007 8 1031 946	-16 727 -818 -18 962 995 -22 938 1017 H. 2. 19	18 508 480 -18 838 -818 20 430 270 22 394 -298 -22 442 -416	-8 239 -145 -10 778 -099 -12 015 -596 14 318 -318 -14 827 -951	-6 434 -177 6 713 -730 -6 1248 1003 10 1248-1387 -10 566 510	7 473 841 -7 340 488 9 374 709 -11 340 -471 -17 499 588
H, 0, 10 0 2181-1952 2 480 70	7 1129 1183 9 459 425 11 1234-1151 13 1618-1423 15 1023 -972	-3 336 -269 -5 889 -825 2 595 635 -7 326 -276 9 1078 1250	-11 403 426 -17 382 302 -19 375 376 -19 1, 23	-8 1810-1896 -10 505 -532 12 1134-1241 -12 671 -681 -14 1302 1431	1 647 -499 -1 530 458 3 417 -355 -3 437 334	-24 273 -169 H, 3, 6 -1 332 314	-16 241 -315 H, 3, 18 1 528 -503	12 461 526 -12 1341-1425 14 624 -707 16 651 614 -10 782 -734	H, 4, 18 0 395 -172 0 417 376
-2 3768-3313 6 090 -043 -4 1768-1415 6 623 624 -6 1835-1623	23 826 -634 H, 1, 1 2 1639-1899	11 412 335 -11 773 801 -13 519 607 -15 624 735 19 369 444	0 362 -334 -2 705 634 -4 278 280 6 485 556	-18 1602-1583 20 590 497 22 590 -501 -22 778 -692 -24 920 910	-3 596 560 -7 671 552 11 311 -340 -15 427 512 -17 600 448	-3 408 -259 -5 472 -639 7 414 -381 -11 412 537 13 441 657	3 376 -278 -3 603 -478 7 559 664 -7 674 396 -9 351 320	-18 1072 1068 20 405 387 -20 491 -473 -22 504 464	10 532 598 -12 772 851 -14 584 -510 -16 680 690
-8 1534 1402 10 409 399 -10 1273-1163 12 855 -948	+ 1848-2501 6 500 686 -6 1+20-1860 8 347 454 -5 711 -794	21 653 670 H, 1, 11	-18 231 216 H, 1, 25 2 400 -430	H, 2, 9 1 1036 926 -1 991 -801	H. 2.20 0 2403 2095 2 2540-2301	H, 3, 7 0 1803 1686	13 +52 -+60 H, 3, 19 -2 190 323	H, 4, 7 1 481-398 -1 687 630 -5 689 -579	H, 4, 19 -3 505 -485 5 255 376
14 818 811 -14 1561-1522 16 2326-2165 -18 1060 -969 20 1055 -892	10 1227 1233 -10 6+1 -608 12 274 -275 14 1614-1601 15 826 710	2 708 720 -2 897 819 - 560 526 - 219 -227 - 5 266 220	4 396 -387 -4 757 782 6 207 219 -6 588 -505 -8 258 -235	3 592 478 -3 918 -706 -5 1309-1141 -7 1062 -970 -9 390 -368	+ 2176 2076 + 2370 1876 6 2449-2448 +6 3639-3108 8 1919 1876	4 200 130 -4 1086 1000 -6 377 345 8 296 341 10 730 960	6 782 849 -6 432 343 8 362 437 -8 447 -387 10 466 439	9 648 -799 -9 563 618 11 577 -714 -11 626 458 -13 317 -318	-5 552 -526 7 243 177 -7 542 -489 -9 526 -499 -11 379 -367
-20 491 420 22 1192 1151 -72 591 -525 -24 702 558 -26 1091 -949	-16 854 -794 18 683 674 -18 298 -253 20 322 227 24 807 -569	8 226 193 -8 340 -215 -10 398 309 -12 703 807 -14 754 792	-12 572 570 H, 1, 26 -13 387 -458	11 443 451 -15 606 -738 17 465 -571 -17 979-1021 -19 617 -605	-8 3722 3213 10 2140-2140 -10 3363-3046 12 1758 1711 -12 2577 2371	-10 741 831 12 256 280 -12 585 753 -14 1027 1126 -20 616 647	-10 249 159 -14 483 421 -20 534 -534 H, 3, 20	-15 744 -030 -17 309 -342 H, 4, 8	H, 4, 20 2 268 -285 -2 860 -892
H, 0, 12 0 944 -717 2 447 574 4 1144 1272	H, 1, 2 3 846 -992 -3 800 800	-16 493 495 -18 575 -488 -22 759 773 -24 344 265 -26 431 353	H, L, 27 0 433 -572 -10 210 -230	H, 2, 10 0 341 515 2 810 011	-14 1755 1750 -18 1240-1324 -20 1365 1510	H, 3, 8	-5 373 326 -7 579 538 -11 410 -384 -15 227 -326 -17 101 366	2 2871-2718 -2 3306-3126 + 2752 2725 -4 4655 4542 6 3038-3191	8 512 -511 -6 323 326 -12 480 -448 -16 482 -401
-6 466 -303 -6 1711 1515 8 885 907 -8 1203-1025 10 617 -636	-5 867 1036 7 675 -882 -7 1337 1747 9 602 -684 -9 1114 1227	H, 1, 12 1 834 737 -1 1154-1055	-12 371 -439 H, 2, 0 4 1646-1830	-2 200 -184 4 1484 1455 -4 296 -184 -6 1658 1419 8 349 389	-1 532 -446 -3 1072 -873 -5 775 -558 7 476 665	-3 380 433 5 339 376 -5 976-1033 7 355 -297 -7 748 -838	H- 3, 21 -2 714 042 -4 348 324	-0 3168-5224 8 2560 3105 -8 3740 3472 10 2500-3183 -10 3782-4489	H, 4, 21 1 620 -758 3 525 -632 -3 318 -377
12 1350 1375 14 951 947 -14 456 -551 18 886 591 -16 1418 1535	11 976 -917 -11 827 890 19 501 -668 -19 775 682 -23 425 310	3 348 343 -3 1178-1000 -5 1136-1021 -7 920 -871 9 346 398	6 352 248 10 958 -790 12 549 507 14 2559-2220 20 888 723	10 610 -757 -10 1033 1009 12 1464 1488 -12 774 -850	-13 368 -488 -17 346 398 H, 2, 22	9 864 -844 -11 831 948 13 555 567 15 598 487 -15 565 -597	+ 103 -212 8 062 728 -8 850 791 -10 391 ++5 -12 50+ 515	12 2384 2031 -12 2343 2450 14 2391-2305 -14 2123-2404 10 2015 2488	-7 651 540 -9 631 624 -13 322 -295 M, 4, 22
-18 1932-1942 -20 805 -666 -22 858 -804 -74 500 436	H, 1, 3 0 2017 2518 2 1251 1+00	11 515 -540 11 513 705 -17 766 -755 -25 273 -342	H. 2. 1 3 337 301	16 519 519 18 1014 -977 -18 1189 1183 20 679 561	-2 592 555 4 540 -532 -4 727 631 6 591 717 -6 667 -563	-17 732 -725 -19 273 -07 -21 440 497 -23 298 307	H, 3, 22 1 238 -256 -1 344 315	-16 1823 1936 18 1907-1328 -18 1941-2001 -20 1538 1140 -22 1477-1108	2 325 - 322 -4 331 271 -6 474 - 559 -10 291 302
0 1284 1067 2 835 667 -2 613 515 4 895 651	- 1137-1210 -6 1137-1210 -6 1065-1216 -8 692 V20 10 835 V89	0 389 -324 2 644 491 -7 2688-2720 -4 350 -489	5 1519 1819 -5 1325-1524 7 1715 2036 -7 457 -498 9 540 657	-22 760 692 -26 777 -767 H. 2. 11	-10 565 -513 -12 818 730 -14 509 -463 -18 762 -694	0 1892-1747 -2 1017-1015 - 408 308	-5 328 -354 -13 325 -316 H, 3, 23	H, 4, 9 1 548 437 -1 1444 1202 3 1033 907	-14 869 702 H. 4. 23 -1 251 382
-4 575 -483 6 961 -834 -6 1477 1372 8 554 497 -8 1137 847	-10 862 1086 12 990 1040 -12 1428 1548 14 241 277 -14 207 -227	-6 712 044 8 (157-1287 -8 983 888 10 485 -571 -10 318 -299	-v 307 308 11 502 -015 -13 3v8 -009 15 865 838 17 1152 1032	-1 510 319 512 -497 -3 1092 828 5 791 -818 -5 979 896	H, 2, 23 -13 435 -504 -15 400 -488	-6 389 299 -8 264 -232 10 1525-1954 -10 969 -966 12 813 -933	0 643 -769 -2 203 -259 -4 644 -591 -8 296 -298 -10 269 -521	-3 2180 1940 -5 1010 802 7 908-1002 9 805 -784 -11 810 865	-11 208 319 H. 4, 24 0 1372 1002
-10 1966 1807 12 1360 1458 14 1024 -902 -14 1254 1161 18 030 -514	-16 958-1022 -18 891 775 26 21 165 -26 613 -572 -26 621 -582	17 777 875 -12 767 -767 -14 820 -419 16 604 -445 -16 291 997	14 572 527 H. 2. 2 2 1211 817	-7 751 693 -9 490 502 15 617 -564 -21 592 424	H. 2, 24 0 559 812 -2 708 540 4 664 451	-12 544 -592 -14 423 200 16 340 -229 -16 940 1059 -18 366 533	-12 189 -181 -14 230 -236 -18 157 -146 M, 3, 24	13 394 519 -13 826 1066 -15 409 474 17 479 -509 -21 457 483	-2 1586-1572 -4 1832 1804 -6 1741-1610 -8 1797 2009 -10 1044-1187
-18 1105 1213 20 723 747 -20 734 -054 -22 1092 1079 -24 518 -521	H, 1, 4 3 025 767 -3 716 -922 5 1386 -922	-18 339 349 -18 339 349 20 218 -231 -20 255 -200 -22 460 -377	-2 -2/3 -344 + 2337 2275 -4 1209-1062 8 900 1117 -8 735 -846 10 1308-1437	H, 2, 12 0 5001 4623	-8 +58 -237 -10 732 -841 +10 350 328	20 495 -303 H, 3, 10 -3 461 537	-13 347 -337 H, 3, 22	H, A, 10 0 1310 1172 2 1385 1009	
					~ () ()	> 001 -031			

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 axi is shown in Fig. 1. Tables 3 and 4 list bond lengths an angles.

All the eight copper ions in the asymmetric un exhibit the usual 4+2 coordination, with bond length in agreement with the generally accepted ones. Th average Cu-O distance in the planar squares forme

Table 3	. Bond	lengths
---------	--------	---------

				0(20) Cu(5
1 x y ii $x + y$	$\frac{z}{z-1}$	$v_1 - x - y$ $v_2 - x - y_+$	$-\frac{1}{2}$ $\frac{1}{2}-Z$	
iii $x \frac{3}{3} - y$	$\frac{z}{z - \frac{1}{2}}$	viii $1-x$ $\frac{1}{2}+$	$-\frac{2}{y} + \frac{2}{1} - \frac{2}{z}$	
iv $x y - 1$	Z	ix $1-x$ $y-$	$-\frac{1}{2}$ $\frac{1}{2}$ $-z$	O(17r) = O(2)
$\mathbf{v} \mathbf{x} 1 + \mathbf{y}$	Z	$x x \frac{1}{2}$	$-y = \frac{1}{2} + z$	O(1/2) - Cu(3)
Cu(1i) = O(17i)	1.96 Å	$C_{11}(2^{i}) = O(18^{i})$	1.94 Å	
$-O(18^{i})$	2.01	$-O(17^{iv})$	1.98	
$-O(28^{ii})$	2.04	$-O(27^{ii})$	2.02	O(21 ⁱ)Cu(3 ⁱ
$-O(27^{iii})$	2.11	$-O(28^{ii})$	2.03	
$-O(19^{i})$	2.26	$-O(14^{ii})$	2.39	
-O(26 ⁱⁱⁱ)	2.33	-O(4 ⁱ)	2.39	O(19 ⁱ)—Cu(3 ⁱ
				$O(4x) = C_{12}(2)$
$Cu(3^{1}) = O(20^{1})$	1.90	$Cu(4^{1}) - O(19^{1})$	1.88	U(4)Cu(3
$-O(1/^{\circ})$	1.9/	$-O(18^{1})$	1.90	
$-O(21^{1})$	1.98	-O(20 ¹)	1.94	$O(21^{i}) - Cu(5^{i})$
-O(19 ¹)	2.00	-O(22 ¹)	2.00	
-O(4 ^v)	2.45	-O(10 ¹)	2.39	
$-O(10^{1})$	2.56	-O(4 ¹)	2.44	
$Cu(5^{i}) - O(21^{i})$	1.90	$Cu(6^{i})-O(22^{i})$	1.89	Q(22i) Cu(5i
$-O(23^{i})$	2.00	$-O(24^{i})$	1.93	$O(23^{-}) - Cu(3^{-})$
$-O(22^{i})$	2.10	$-O(23^{iv})$	2.07	
$-O(24^{i})$	2.12	$-O(21^{iv})$	2.11	
$-O(25^{i})$	2.37	$-O(8^{iv})$	2.38	O(22i) - Cu(5)
$-O(10^{i})$	2.37	-O(20 ⁱ)	2.43	O(22)Cu(5
$C_{\rm ev}(7i)$ $O(24i)$	1.07		1.05	
$Cu(7) = O(24^{1})$	1.96	$Cu(8^{1}) - O(26^{1})$	1.85	$O(24^{i})-Cu(5^{i})$
$-O(25^{2})$	1.97	-0(25)	1.91	
$-O(26^{-1})$	2.05	$-O(23^{-1})$	2.05	$O(25^{1}) - Cu(5^{2})$
-O(14i)	2.00	-O(27)	2.03	
-O(8iv)	2.31	$-0(3^{-})$	2.44	$O(24^{i}) - Cu(7)$
-0(8')	24)	-0(1+*)	2.42	-()(-
$Ca(1^{i}) - O(30^{v_{i}})$	2.28	$Ca(2^{i})-O(11^{viii})$	2.32	
-O(5 ⁱ)	2.31	-O(13 ^{vi1i})	2.35	
$-O(3^{i})$	2.35	-O(33 ⁱ)	2.39	
$-O(31^{vi})$	2.36	$-\mathbf{O}(\mathbf{34^{ix}})$	2.39	$O(25^{1}) - Cu(7)$
-O(29 ⁱ)	2.37	$-O(32^{i})$	2.53	
$-O(7^{vii})$	2.40	-O(9 ⁱ)	2.53	
-O(6 ^{vi})	2.54	-O(12 ⁱ)	2.57	
0(11) 0(41)			1.30	$O(26^{10}) - Cu(7)$
$S(1^{+}) - O(4^{+})$	1.44	$S(2^{1}) - O(6^{1^{v}})$	1.38	
$-O(1^{11})$	1.48	-O(5 ¹)	1.4/	O(28i) - Cu(7i)
$-O(3^{1})$	1.51	-0(81)	1.48	0(20)—Cu(7
-0(2**)	1.24	-U(/*)	1.20	O(14 ⁱ)Cu(7 ⁱ
S(3 ⁱ)—O(9 ⁱ)	1.44	$S(4^{i}) - O(16^{i})$	1.47	
-O(10 ⁱ)	1.44	-O(14 ⁱ)	1.48	O(30vi)-Ca(1
$-O(11^{i})$	1.53	$-O(13^{i})$	1.51	- (, -)"
-O(12 ⁱ)	1.56	-O(15x)	1.52	
- /		· · ·		

Estimated standard deviations for Ca-O, Cu-O and Sbond lengths are ≤ 0.04 Å.

Table	4.	Bond	angles
-------	----	------	--------

	O(17 ⁱ)—Cu(1 ⁱ)–O(18 ⁱ) 99° –O(28 ⁱⁱ) 178	$O(18^{i})$ — $Cu(2^{i})$ – $O(17^{iv})$ - $O(27^{ii})$	106° 172
	$-O(27^{111})$ 79	$-O(28^{ii})$	82
:.	$-O(19^{1})$ /6 $-O(26^{111})$ 101	$-O(14^{1})$ $-O(4^{1})$	83
.1S	$O(18^{i}) - Cu(1^{i}) - O(28^{ii})$ 80	$O(17^{i})$ Cu(2 ⁱ)-O(27 ⁱⁱ)	81
a	$-O(27^{iii})$ 177	$-O(28^{ii})$	171
it	$-O(19^{4})$ /2 $-O(26^{111})$ 105	$-O(14^{11})$ $-O(4^{11})$	99 88
ns	$O(28^{i})$ — $Cu(1^{i})$ - $O(27^{iii})$ 103	$O(27^{ii}) - Cu(2^{i}) - O(28^{ii})$	91
ne	$-O(19^{i})$ 104	$-O(14^{ii})$	87
ed	$O(27^{iii})-Cu(1^{i})-O(19^{i})$ 107	$O(28^{ii}) - Cu(2^{i}) - O(14^{ii})$	92 85
	$-O(26^{111})$ 75	-O(4 ⁱ)	88
	$O(19^{i})$ Cu(1 ⁱ)-O(26 ⁱⁱⁱ) 176	$O(14^{ii}) - Cu(2^{i}) - O(4^{i})$	173
	O(20i) $O(2i)$ $O(17v)$ 00	$O(10i)$ $O_{1}(4i)$ $O(18i)$	01
- 7	$-O(21^{i})$ 88	$O(19^{-1}) - O(18^{-1}) - O(20^{-1})$	175
- Z - 7	$-O(19^{i})$ 176	$-O(22^{i})$	92
- z	-O(4 ^v) 89	-O(10 ⁱ)	93
- <i>z</i>	$-O(10^{1})$ 91	$-O(4^{1})$	87
- <i>z</i>	$O(1/^{\circ}) - Cu(3^{\circ}) - O(21^{\circ}) = 1/3$	$O(18^{1}) - Cu(4^{1}) - O(20^{1})$	9/
2	$-O(19^{-}) = 82$ $-O(4^{-}) = 86$	$-O(22^{-})$	104
A	$-O(10^{i})$ 100	$-\Omega(10)$	83
	$O(21^{i})$ — $Cu(3^{i})$ - $O(19^{i})$ 91	$O(20^{i})$ — $Cu(4^{i})$ – $O(22^{i})$	87
	-O(4 ^v) 94	-O(10 ⁱ)	92
	-O(10 ⁱ) 80	-O(4 ⁱ)	88
	$O(19^{i})$ — $Cu(3^{i})$ - $O(4^{v})$ 95	$O(22^{i})$ $Cu(4^{i})$ $O(10^{i})$	82
	$-O(10^{i}) = 85$ $O(4^{v})$ $Cu(3^{i})$ - $O(10^{i}) = 174$	$-O(4^{i})$ $O(10^{i})$ $Cu(4^{i})$ - $O(4^{i})$	90 173
			1.0
	$O(21^{i}) - Cu(5^{i}) - O(23^{i}) = 84$	$O(22^{i}) - Cu(6^{i}) - O(24^{i})$	86
	-O(22 ⁱ) 98	-O(23 ^{iv})	179
	-O(24 ⁱ) 174	-O(21 ^{iv})	102
	$-O(25^{i})$ 109	$-O(8^{iv})$	96
	$-O(10^{1})$ 87	$-O(20^{1})$	77
	$O(23^{1}) - Cu(5^{1}) - O(22^{1}) = 1/6$	$O(24^{1}) - Cu(6^{1}) - O(23^{1}v)$	172
	$-O(24^{2})$ 102 -O(25i) 77	$-O(21^{-1})$	86
	$-O(10^{i})$ 96	$-O(20^{i})$	110
	$O(22^{i})$ Cu(5 ⁱ)-O(24 ⁱ) 76	$O(23^{iv})$ — $Cu(6^{i})$ – $O(21^{iv})$	77
	-O(25 ⁱ) 106	-O(8 ^{iv})	84
	-O(10 ⁱ) 81	-O(20 ⁱ)	102
	$O(24^{1})$ — $Cu(5^{1})$ – $O(25^{1})$ 74	$O(21^{1v}) - Cu(6^{1}) - O(8^{1v})$	92
	$-O(10^4)$ 91 $O(25i)$ $C_{10}(5i)$ $O(10i)$ 161	$-O(20^{\circ})$ O(8ix) = Cy(6i) = O(20i)	161
	$O(23^{-}) = O(10^{-})^{-} O(10^{-})^{-} 101$	$O(3^{-1}) Cu(0^{-}) - O(20^{-})$	101
	$O(24^{i})$ — $Cu(7^{i})$ – $O(25^{i})$ 88	$O(26^{i})$ — $Cu(8^{i})$ – $O(25^{i})$	177
	$-O(26^{iv})$ 92	-O(23 ⁱ)	93
	-O(28 ⁱ) 176	-O(27 ⁱ)	87
	$-O(14^{i})$ 91	$-O(8^{i})$	94
	$-O(8^{1v})$ 83 O(25i) $O(2(iv)$ 170	$-O(14^{1})$	93
	$O(25^{\circ}) - Cu(7^{\circ}) - O(26^{\circ}) = 1/9$	$O(25^{1}) - Cu(8^{1}) - O(23^{1})$	89
	$-O(14^{i})$ 89	-O(2i)	89
	$-O(8^{iv})$ 93	-O(14 ⁱ)	85
	$O(26^{iv}) - Cu(7^{i}) - O(28^{i}) 86$	$O(23^{i})$ — $Cu(8^{i})$ – $O(27^{i})$	175
	$-O(14^{i})$ 90	-O(8 ⁱ)	84
	$-O(8^{iv})$ 88	$-O(14^{i})$	92
	$U(23^{+}) - U(1^{+}) - U(14^{+}) = 86$ - $O(2iv) = 100$	$O(2/2) \longrightarrow O(8^2) \longrightarrow O(1/4^3)$	101
	$O(14^{i})$ - $Cu(7^{i})$ - $O(8^{iv})$ 173	$O(8^{i})$	172
	$O(30^{vi})-Ca(1^{i})-O(5^{i})$ 98 $O(2^{i})$ 98	$O(11^{viii})-Ca(2^{i})-O(13^{viii})$	80
	-O(31vi) 78	-O(34ix)	84
	$-O(29^{i})$ 170	$-O(32^{i})$	166
-0	$-O(7^{vii})$ 105	-O(9 ⁱ)	122
	$-O(6^{vi})$ 80	-O(12 ⁱ)	82

	· · ·	
$O(5^{i})Ca(1^{i}) - O(3^{i})$ 80	$O(13^{viii})-Ca(2^{i})-O(33^{i})$	92
-O(31 ^{vi}) 159	$-O(34^{ix})$	- 78
-O(29 ⁱ) 90	-O(32i)	87
-O(7 ^{vii}) 123	-O(9 ⁱ)	146
-O(6 ^{vi}) 80	$-O(12^{i})$	158
O(3i)Ca(1i)-O(31vi) 80	$O(33^{i})$ — $Ca(2^{i})$ – $O(34^{ix})$	168
-O(29 ¹) 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	$O(5^{i})$	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	$-\mathbf{O}(\mathbf{15^{ix}})$	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

Table 4 (cont.)

Estimated standard deviations for O-Cu-O and O-Ca-O angles are $\leq 1^{\circ}$ and for O-S-O angles are $\leq 2^{\circ}$.

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 ${}_{\infty}^{2}[Cu_{2}(OH)_{3}O]^{-}$. 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 SO₄²⁻ 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 nonequivalent 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	e 5.	Hyd	rogen	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(9i) - O(33iv)	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
$O(16^{i}) - O(32^{i})$	2.64
$O(21^{i}) - O(29^{i})$	2.96
$O(23^{i}) - O(34^{i})$	2.68
O(2i) = O(10i)	2.04
O(5) = O(19)	2.05
$O(3^{1}) - O(22^{1})$	3.02

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

$$Ca_2Cu_5Zn(Zn_{0.88}Cu_{0.12})_2(OH)_{12}(SO_4)_4.6H_2O$$

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. A 25, 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.

Acta Cryst. (1972). B28, 1189

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

(Received 30 September 1971)

The structure of *cis*-4-t-butylcyclohexane-1-carboxylic acid, $C_{11}O_2H_{20}$, has been determined from threedimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit cell, of dimensions $a = 17 \cdot 132$, $b = 6 \cdot 271$, $c = 10 \cdot 380$ Å and $\beta = 92 \cdot 17^{\circ}$, contains four molecules. The structure has been solved using a symbolic phasing procedure and Fourier synthesis. Refinement by the least-squares (blockdiagonal approximation) method converged to a final *R* index of $5 \cdot 7\%$ 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 $2 \cdot 640$ Å. The axial carboxyl group is nearly coplanar with an α,β -bond in the ring (torsion angle = $6 \cdot 4^{\circ}$), 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 $\pm 17^{\circ}$;

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):