

Table 2. Bond distances (Å) and angles (°)

|                | $\alpha$  | $\beta$   |                  | $\alpha$  | $\beta$   |
|----------------|-----------|-----------|------------------|-----------|-----------|
| Cu—O(1)        | 1.989 (2) | 1.966 (2) | C(3)—H(31)       | 1.12 (5)  | 0.99 (6)  |
| Cu—N(1)        | 2.022 (3) | 2.002 (3) | C(3)—H(32)       | 0.96 (4)  | 1.00 (5)  |
| Cu—O(3)        | 2.401 (3) | 2.611 (4) | C(4)—H(41)       | 0.97 (5)  | 0.99 (5)  |
| C(1)—O(1)      | 1.281 (5) | 1.275 (4) | C(4)—H(42)       | 0.97 (5)  | 1.10 (5)  |
| C(1)—O(2)      | 1.221 (5) | 1.229 (5) | C(5)—H(51)       | 0.95 (5)  | 0.92 (5)  |
| C(1)—C(2)      | 1.507 (6) | 1.520 (6) | C(5)—H(52)       | 0.94 (5)  | 0.90 (5)  |
| C(2)—N(1)      | 1.484 (5) | 1.460 (6) | C(6)—H(61)       | 0.83 (5)  | 0.80 (6)  |
| C(2)—C(3)      | 1.520 (6) | 1.492 (6) | C(6)—H(62)       | 1.13 (5)  | 1.02 (5)  |
| C(3)—C(4)      | 1.516 (8) | 1.488 (7) | O(3)—H(7)        | 0.87 (5)  | 0.68 (6)  |
| C(4)—C(5)      | 1.507 (7) | 1.511 (8) | O(1)...H(7)*     | 1.96 (5)  | 2.43 (6)  |
| C(5)—C(6)      | 1.518 (7) | 1.516 (7) | O(1)...O(3)      | 2.825 (4) | 3.066 (5) |
| C(6)—N(1)      | 1.470 (5) | 1.451 (6) | O(3)—H(8)        | 0.60 (5)  | 0.81 (5)  |
| N(1)—H(1)      | 0.91 (5)  | 0.98 (5)  | O(1)...H(8)      | 2.26 (5)  | 3.45 (6)  |
| C(2)—H(2)      | 1.19 (5)  | 1.28 (5)  | O(1)...O(3)      | 2.837 (4) | —         |
| O(1)—Cu—N(1)   | 83.1 (1)  | 84.1 (1)  | N(1)—C(6)—C(5)   | 112.3 (4) | 113.0 (4) |
| O(1)—Cu—O(3)   | 90.4 (1)  | 93.0 (1)  | C(2)—N(1)—C(6)   | 111.3 (3) | 113.6 (4) |
| N(1)—Cu—O(3)   | 90.6 (1)  | 90.5 (1)  | H(7)—O(3)—H(8)   | 108 (7)   | 97 (7)    |
| Cu—O(1)—C(1)   | 114.6 (2) | 114.2 (2) | C(1)—C(2)—H(2)   | 116 (2)   | 105 (2)   |
| Cu—N(1)—C(2)   | 105.0 (2) | 105.8 (3) | C(6)—N(1)—H(1)   | 116 (3)   | 110 (3)   |
| O(1)—C(1)—C(2) | 115.6 (3) | 115.8 (3) | H(31)—C(3)—H(32) | 110 (4)   | 116 (4)   |
| O(2)—C(1)—C(2) | 120.3 (4) | 120.8 (4) | H(41)—C(4)—H(42) | 117 (4)   | 107 (4)   |
| N(1)—C(2)—C(1) | 110.5 (3) | 110.2 (4) | H(51)—C(5)—H(52) | 118 (4)   | 98 (5)    |
| N(1)—C(2)—C(3) | 112.3 (4) | 114.6 (4) | H(61)—C(6)—H(62) | 108 (4)   | 104 (5)   |
| C(2)—C(3)—C(4) | 109.5 (4) | 111.9 (4) | O(3)—H(7)...O(1) | 172.8 (5) | 157.1 (7) |
| C(3)—C(4)—C(5) | 112.2 (4) | 113.5 (4) | O(3)—H(8)...O(1) | 168.1 (8) | —         |
| C(4)—C(5)—C(6) | 112.5 (4) | 114.1 (4) |                  |           |           |

\* The dotted line represents a bond between atoms in different molecules.

Table 3. Torsion angles (°) (*e.s.d.*'s ~ 0.4°)

|                   | $\alpha$ | $\beta$ |
|-------------------|----------|---------|
| N(1)C(2)—C(3)C(4) | 56.47    | 51.03   |
| C(2)C(3)—C(4)C(5) | -52.85   | -46.73  |
| C(3)C(4)—C(5)C(6) | 51.16    | 45.14   |
| C(4)C(5)—C(6)N(1) | -51.65   | -46.01  |
| C(5)C(6)—N(1)C(2) | 54.48    | 49.49   |
| C(6)N(1)—C(2)C(3) | -57.91   | -53.09  |

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## Calcium D-Glucarate Tetrahydrate, $\text{Ca}^{2+} \cdot \text{C}_6\text{H}_8\text{O}_8^{2-} \cdot 4\text{H}_2\text{O}$ : a Redetermination

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**Abstract.**  $M_r = 320.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 16.220$  (2),  $b = 11.347$  (2),  $c = 6.558$  (1) Å,  $V = 1207.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.76$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 49.65$  cm<sup>-1</sup>,  $F(000) = 672$ ,  $T = 293$  K,  $R = 0.0514$  for 1012 observed reflections. The results have been compared with the original study of Taga & Osaki [*Bull. Chem. Soc. Jpn* (1976), **49**, 1517–1520], and show agreement with improved accuracy. The hydrogen positions have now been determined and a complete description of the hydrogen-bonding scheme is given.

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the analogous compound, calcium D-galactarate, and with other calcium-coordinated carbohydrates.

**Experimental.** Prepared from K gluconate and CaCl<sub>2</sub> solutions; crystal 0.1 × 0.1 × 0.3 mm, Enraf-Nonius CAD-4F diffractometer, Cu Kα radiation, cell dimensions calculated from  $\theta$  measurements of 36 reflections. 3629 reflections measured,  $2\theta_{\max} = 120^\circ$ ,  $h - 19 \rightarrow 19$ ,  $k - 13 \rightarrow 13$ ,  $l 0 \rightarrow 8$ , data merged using SHELX76 (Sheldrick, 1976) giving 1040 unique reflections,  $R_{\text{int}} = 0.0600$ , 1012 [ $I > 3\sigma(I)$ ] used in analysis. As an intensity check the 720 reflection was used: average count 1306 and  $\sigma$  (calculated from the distribution) = 70.9 (5.4%). No absorption correction applied. MULTAN80 (Main *et al.*, 1980) used to solve structure and least-squares refinement carried out, with SHELX, for the positional parameters for all atoms except the H atoms of the water molecules;  $\sum w(\Delta F)^2$  minimized,  $w = 1/(\sigma^2 F + 0.007411F^2)$ ; H atoms located from difference Fourier synthesis;  $R = 0.0514$ ,  $wR = 0.0792$ . In final SFLS cycle max. shift/error 0.02, av. 0.004; on final difference Fourier synthesis max. and min. electron densities 0.33 and  $-0.39 \text{ e } \text{Å}^{-3}$ ; scattering factors from *International Tables for X-ray Crystallography* (1974). Figures drawn with PLUTO78 (Motherwell & Clegg, 1978).

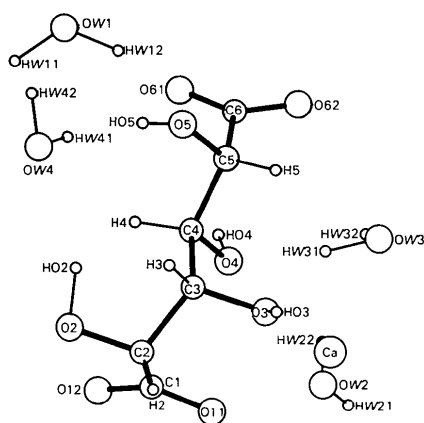


Fig. 1. View of the structure showing the numbering scheme.

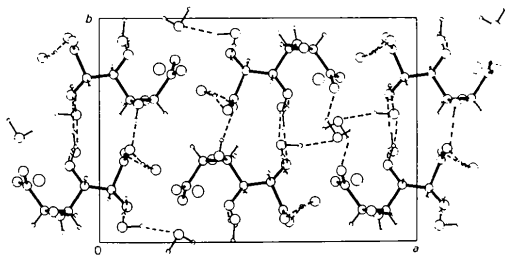


Fig. 2. *c*-axis-projection packing diagram.

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{Å}^2 \times 10^4$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | <i>x</i> | <i>y</i> | <i>z</i>  | <i>U</i> <sub>eq</sub> |
|-------|----------|----------|-----------|------------------------|
| Ca    | 3102 (1) | 2261 (1) | 8605 (2)  | 394                    |
| C(1)  | 2724 (4) | 2496 (6) | 3535 (11) | 397                    |
| C(2)  | 3273 (4) | 3602 (6) | 3276 (10) | 366                    |
| C(3)  | 4025 (4) | 3638 (6) | 4700 (11) | 379                    |
| C(4)  | 4534 (4) | 2505 (5) | 4647 (11) | 402                    |
| C(5)  | 5379 (4) | 2673 (6) | 5646 (11) | 396                    |
| C(6)  | 5769 (3) | 1414 (6) | 5870 (12) | 416                    |
| O(11) | 2418 (2) | 2337 (5) | 5247 (8)  | 472                    |
| O(12) | 2615 (3) | 1862 (4) | 2041 (8)  | 468                    |
| O(2)  | 3552 (3) | 3649 (4) | 1198 (8)  | 442                    |
| O(3)  | 3773 (3) | 3824 (4) | 6754 (7)  | 432                    |
| O(4)  | 4083 (3) | 1633 (4) | 5758 (9)  | 491                    |
| O(5)  | 5855 (2) | 3419 (4) | 4375 (10) | 541                    |
| O(61) | 5965 (3) | 876 (5)  | 4309 (9)  | 562                    |
| O(62) | 5807 (3) | 1037 (5) | 7664 (9)  | 543                    |
| O(W1) | 6788 (3) | 1783 (6) | 1028 (9)  | 670                    |
| O(W2) | 2480 (4) | 373 (5)  | 8393 (14) | 779                    |
| O(W3) | 4250 (3) | 1046 (5) | 9999 (10) | 607                    |
| O(W4) | 5743 (5) | 4290 (7) | 232 (16)  | 989                    |

Table 2. Bond distances ( $\text{Å}$ ) and angles ( $^\circ$ )

|                  |           |                  |           |
|------------------|-----------|------------------|-----------|
| C(1)–C(2)        | 1.549 (8) | C(2)–O(2)        | 1.437 (8) |
| C(2)–C(3)        | 1.537 (9) | C(3)–O(3)        | 1.424 (8) |
| C(3)–C(4)        | 1.528 (9) | C(4)–O(4)        | 1.430 (9) |
| C(4)–C(5)        | 1.531 (9) | C(5)–O(5)        | 1.418 (9) |
| C(5)–C(6)        | 1.569 (9) | C(6)–O(61)       | 1.233 (9) |
| C(1)–O(11)       | 1.240 (8) | C(6)–O(62)       | 1.253 (9) |
| C(1)–O(12)       | 1.228 (8) |                  |           |
| O(12)–C(1)–O(11) | 125.4 (6) | C(5)–C(4)–C(3)   | 111.7 (5) |
| C(2)–C(1)–O(11)  | 116.5 (6) | O(4)–C(4)–C(3)   | 107.1 (5) |
| C(2)–C(1)–O(12)  | 118.0 (6) | O(4)–C(4)–C(5)   | 109.1 (5) |
| O(2)–C(2)–C(1)   | 108.4 (5) | C(4)–C(5)–O(5)   | 108.1 (6) |
| C(3)–C(2)–C(1)   | 114.3 (5) | C(6)–C(5)–O(5)   | 112.3 (5) |
| C(3)–C(2)–O(2)   | 108.9 (5) | C(6)–C(5)–C(4)   | 106.7 (5) |
| O(3)–C(3)–C(2)   | 110.5 (5) | C(5)–C(6)–O(61)  | 118.5 (7) |
| C(4)–C(3)–C(2)   | 113.1 (6) | O(62)–C(6)–O(61) | 126.7 (7) |
| C(4)–C(3)–O(3)   | 107.6 (5) | O(62)–C(6)–C(5)  | 114.8 (6) |

**Discussion.** Fig. 1 shows the structure with the labelling scheme. Fig. 2 is a packing diagram along *c*. Atom coordinates and equivalent isotropic temperature factors are given in Table 1,\* and bond lengths and angles in Table 2. The calcium coordination scheme is in agreement with that proposed by Taga & Osaki (1976). The Ca<sup>2+</sup> ion is surrounded by eight O atoms in a distorted square antiprism arrangement. All the O–Ca distances lie in the range 2.37 (1)–2.55 (1) (average = 2.45 Å). This average value compares with values given by Dheu-Andries & Perez (1983) of 2.48 Å for Ca–O and 2.42 Å for Ca–O(W); corresponding values for calcium gluconate tetrahydrate are 2.46 and 2.42 Å.

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and details of the hydrogen bonding and calcium coordination have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39974 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of results*

|                      | Taga & Osaki<br>(1976) | This<br>determination |
|----------------------|------------------------|-----------------------|
| Calcium coordination | 2.458 (63) Å           | 2.445 (57) Å          |
| Bond lengths:        |                        |                       |
| C—C                  | 1.540 (26)             | 1.543 (17)            |
| Hydroxyl C—O         | 1.443 (20)             | 1.427 (8)             |
| Carboxyl C—O         | 1.257 (24)             | 1.239 (11)            |
| Bond angles:         |                        |                       |
| Tetrahedral C        | 112.0 (3.5)°           | 111.6 (3.9)°          |
| Trigonal C           | 127.1 (1.5)            | 126.1 (0.9)           |

These eight O atoms involve two carboxyl O atoms O(11) and O(12) (of different molecules), three hydroxyl O atoms O(2), O(3) and O(4) and those of three of the water molecules. The O atoms of the second carboxyl group, O(61) and O(62), are not directly involved in calcium coordination, but they are hydrogen-bonded to O(W1) *via* H(W12) and H(W11) respectively, and through this to the Ca<sup>2+</sup> ion. Similarly, hydroxyl O(5) is not coordinated, but is hydrogen-bonded to O(W4) *via* H(W41). This is the only water not involved in calcium coordination, but is itself hydrogen-bonded *via* H(W42) to water molecule O(W2). O(5) is also hydrogen-bonded to O(W3), which is involved in calcium coordination. Therefore, the overall calcium coordination combines with the hydrogen bonding to ensure that each O atom is directly or indirectly bound to the cation.

The hydrogen-bonding scheme is shown in Fig. 2. There are no intramolecular hydrogen bonds, but intermolecular hydrogen bonds including the water molecules stabilize the arrangement. This study has enabled a comparison to be made between the results presented

here and those of Taga & Osaki (1976). Comparison of atom coordinates of the non-H atoms shows very little difference though the errors in those given in this paper are, on average, halved compared with the original study. Thus, calcium-coordination distances, bond lengths and bond angles show slight differences only. These are shown in Table 3, figures in parentheses being the variance of the samples. This shows the overall improvement of the data, and verification of Taga & Osaki's (1976) results. The determination of H-atom positions has enabled a clear specification of the hydrogen-bonding scheme to be made.

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### Structure of *trans*-Dichlorobis[3,4,5,6-tetrafluoro-*o*-phenylenebis(dimethylphosphine)]iron(III) Tetrafluoroborate, [FeCl<sub>2</sub>(C<sub>10</sub>H<sub>12</sub>F<sub>4</sub>P<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub>

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**Abstract.**  $M_r = 753.8$ , monoclinic,  $C2/c$ ,  $a = 19.194$  (4),  $b = 11.748$  (5),  $c = 13.416$  (3) Å,  $\beta = 100.50$  (2)°,  $U = 2974.5$  (25) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (floatation) = 1.70 (2),  $D_x = 1.683$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.93$  mm<sup>-1</sup>,  $F(000) = 1508$ , room tem-

perature,  $R = 0.049$  for 1687 observed reflections. The iron atom is *trans* octahedrally coordinated and is located on a crystallographic centre of symmetry, with bond lengths Fe—P 2.292 (1), 2.295 (1), Fe—Cl 2.234 (1) Å and the BF<sub>4</sub><sup>-</sup> anions are disordered. The cation structure is very similar to those of  $[M\{o-C_6H_4(PMe_2)_2\}_2Cl_2]^{n+}$  ( $M = Mn, Co$ ).

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