

## Structure of Calcium Acetate Monohydrate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$

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**Abstract.**  $M_r = 176.18$ , triclinic,  $P\bar{1}$ ,  $a = 6.750$  (5),  $b = 11.076$  (8),  $c = 11.782$  (9) Å,  $\alpha = 116.49$  (5),  $\beta = 92.40$  (9),  $\gamma = 97.31$  (8)°,  $U = 777$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.506$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 7.5$  cm<sup>-1</sup>,  $T = 295$  K,  $F(000) = 368$ ,  $R = 0.037$  for 2057 observed reflections with  $I > 2.5\sigma(I)$ . The structure consists of infinite multiple O-bridged double-stranded Ca chains that are cross-linked *via* an extensive hydrogen-bonding network.

**Introduction.** Recently we studied the crystal structure of the double salt  $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$  (Klop, Duisenberg & Spek, 1983). In order to understand its incongruently saturating properties, it is considered to be relevant to have a knowledge of the crystal structures of the corresponding mono salts. It turned out that the crystal structures of  $\text{Ca}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$  ( $n = 0.5, 1$ ) have not been studied previously, probably

because of the poor crystals that are usually obtained. The present communication reports the crystal structure of  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ .

**Experimental.** Good-quality single crystals obtained by slowly increasing the temperature of a solution of anhydrous  $\text{Ca}(\text{OAc})_2$ , saturated at 273 K, from 269 to 293 K, making use of the retrograde solubility;  $D_m$  not determined. Colourless, transparent, needle-shaped specimen  $0.08 \times 0.13 \times 1.13$  mm mounted inside a sealed Lindemann capillary (to avoid decay due to loss of crystal water). Enraf–Nonius CAD-4F diffractometer. Cell parameters calculated from the setting angles of twelve reflections. Unique data set ( $+h, \pm k, \pm l$ ) with  $0.1 < \theta < 25^\circ$  obtained using the  $\omega/2\theta$ -scan mode with Zr-filtered Mo  $K\alpha$  radiation; total of 3025 reflections scanned; fluctuations in intensity less than 3% as monitored by two reference reflections (013 and 055); intensity data corrected for Lorentz and polarization effects but not for absorption; unique set of

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Table 1. Final coordinates and equivalent isotropic thermal parameters

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

|        | <i>x</i>    | <i>y</i>    | <i>z</i>    | $U_{\text{eq}}(\text{Å}^2)$ |
|--------|-------------|-------------|-------------|-----------------------------|
| Ca(1)  | 0.2263 (1)  | 0.0572 (1)  | -0.0726 (1) | 0.0239 (2)                  |
| Ca(2)  | 0.4048 (1)  | 0.1731 (1)  | 0.2904 (1)  | 0.0223 (2)                  |
| O(1)   | 0.0961 (4)  | -0.1083 (3) | 0.0054 (2)  | 0.0327 (8)                  |
| O(2)   | 0.4093 (4)  | -0.0438 (2) | 0.0916 (2)  | 0.0314 (7)                  |
| O(3)   | 0.4341 (5)  | 0.4095 (2)  | 0.3133 (2)  | 0.0456 (9)                  |
| O(4)   | 0.3565 (4)  | 0.2425 (2)  | 0.1211 (2)  | 0.0323 (7)                  |
| O(5)   | 0.2276 (5)  | 0.1786 (3)  | -0.1851 (3) | 0.053 (1)                   |
| O(6)   | 0.3780 (5)  | 0.1730 (3)  | -0.3481 (3) | 0.062 (1)                   |
| O(7)   | -0.0519 (3) | -0.1330 (2) | -0.2637 (2) | 0.0349 (8)                  |
| O(8)   | 0.2666 (3)  | -0.1511 (2) | -0.2532 (2) | 0.0354 (7)                  |
| O(9)   | 0.4658 (5)  | 0.3125 (3)  | 0.5130 (2)  | 0.047 (1)                   |
| O(10)  | 0.3790 (6)  | 0.0100 (3)  | 0.3697 (3)  | 0.055 (1)                   |
| C(1)   | 0.2511 (5)  | -0.1316 (3) | 0.0489 (3)  | 0.0222 (9)                  |
| C(2)   | 0.2480 (7)  | -0.2669 (4) | 0.0480 (5)  | 0.051 (2)                   |
| C(3)   | 0.3767 (6)  | 0.3680 (3)  | 0.1989 (3)  | 0.034 (1)                   |
| C(4)   | 0.330 (1)   | 0.4651 (4)  | 0.1485 (5)  | 0.070 (2)                   |
| C(5)   | 0.2459 (7)  | 0.2046 (5)  | -0.2750 (5) | 0.060 (2)                   |
| C(6)   | 0.101 (1)   | 0.288 (1)   | -0.293 (1)  | 0.230 (9)                   |
| C(7)   | 0.0875 (5)  | -0.1999 (4) | -0.3007 (3) | 0.033 (1)                   |
| C(8)   | 0.0450 (8)  | -0.3454 (5) | -0.4001 (6) | 0.088 (2)                   |
| H(19)  | 0.445 (9)   | 0.268 (6)   | 0.547 (5)   | 0.08 (1)†                   |
| H(29)  | 0.508 (8)   | 0.394 (6)   | 0.554 (5)   | 0.08 (1)†                   |
| H(110) | 0.454 (9)   | -0.051 (6)  | 0.350 (5)   | 0.08 (1)†                   |
| H(210) | 0.336 (8)   | 0.046 (6)   | 0.441 (6)   | 0.08 (1)†                   |

†  $U_{\text{iso}}$ .

Table 2. Relevant data on the geometry of  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$

| (a) Bond distances (Å)              |           |                             |            |
|-------------------------------------|-----------|-----------------------------|------------|
| Ca(1)–O(1)                          | 2.477 (3) | Ca(2)–O(10)                 | 2.368 (4)  |
| Ca(1)–O(1 <sup>III</sup> )          | 2.396 (3) | O(1)–C(1)                   | 1.251 (4)  |
| Ca(1)–O(2)                          | 2.933 (3) | O(2)–C(1)                   | 1.262 (4)  |
| Ca(1)–O(2 <sup>II</sup> )           | 2.496 (3) | O(3)–C(3)                   | 1.240 (5)  |
| Ca(1)–O(4)                          | 2.321 (3) | O(4)–C(3)                   | 1.263 (4)  |
| Ca(1)–O(5)                          | 2.270 (4) | O(5)–C(5)                   | 1.222 (7)  |
| Ca(1)–O(7)                          | 2.728 (2) | O(6)–C(5)                   | 1.239 (6)  |
| Ca(1)–O(8)                          | 2.399 (2) | O(7)–C(7)                   | 1.244 (4)  |
| Ca(2)–O(2)                          | 2.503 (2) | O(8)–C(7)                   | 1.255 (4)  |
| Ca(2)–O(3)                          | 2.490 (2) | C(1)–C(2)                   | 1.491 (6)  |
| Ca(2)–O(4)                          | 2.460 (3) | C(3)–C(4)                   | 1.500 (6)  |
| Ca(2)–O(7 <sup>III</sup> )          | 2.348 (2) | C(5)–C(6)                   | 1.497 (12) |
| Ca(2)–O(8 <sup>II</sup> )           | 2.301 (2) | C(7)–C(8)                   | 1.490 (7)  |
| Ca(2)–O(9)                          | 2.360 (3) |                             |            |
| (b) O-bridged Ca...Ca distances (Å) |           |                             |            |
| Ca(1)–Ca(1 <sup>III</sup> )         | 3.905 (1) | Ca(1)–Ca(2 <sup>II</sup> )  | 3.950 (1)  |
| Ca(1)–Ca(1 <sup>II</sup> )          | 4.559 (1) | Ca(1 <sup>III</sup> )–Ca(2) | 4.660 (1)  |
| Ca(1)–Ca(2)                         | 3.958 (2) |                             |            |
| (c) Bond angles (°)                 |           |                             |            |
| O(1)–C(1)–O(2)                      | 121.3 (3) | O(5)–C(5)–C(6)              | 116.4 (7)  |
| O(1)–C(1)–C(2)                      | 118.9 (3) | O(6)–C(5)–C(6)              | 117.8 (8)  |
| O(2)–C(1)–C(2)                      | 119.9 (3) | O(7)–C(7)–O(8)              | 122.2 (4)  |
| O(3)–C(3)–O(4)                      | 120.9 (3) | O(7)–C(7)–C(8)              | 120.5 (3)  |
| O(3)–C(3)–C(4)                      | 121.1 (3) | O(8)–C(7)–C(8)              | 117.2 (4)  |
| O(4)–C(3)–C(4)                      | 118.0 (4) | H(19)–O(9)–H(29)            | 120 (7)    |
| O(5)–C(5)–O(6)                      | 125.7 (5) | H(110)–O(10)–H(210)         | 124 (6)    |

Table 2 (cont.)

(d) Hydrogen bonds (Å and °)

|                                    | O...O     | O—H      | H...O    | ∠O—H...O | ∠H...O—X | X                   |
|------------------------------------|-----------|----------|----------|----------|----------|---------------------|
| O(9)—H(19)...O(6 <sup>ii</sup> )   | 2.742 (5) | 0.77 (7) | 1.98 (7) | 173 (6)  | 121 (2)  | C(5 <sup>ii</sup> ) |
| O(9)—H(29)...O(3 <sup>v</sup> )    | 2.803 (4) | 0.81 (6) | 2.01 (6) | 166 (6)  | 126 (2)  | C(3 <sup>v</sup> )  |
| O(10)—H(110)...O(6 <sup>iv</sup> ) | 2.699 (5) | 0.86 (6) | 1.86 (6) | 166 (7)  | 122 (2)  | C(5 <sup>iv</sup> ) |
| O(10)—H(210)...O(6 <sup>ii</sup> ) | 2.994 (5) | 0.83 (7) | 2.23 (7) | 153 (5)  | 127 (2)  | C(5 <sup>ii</sup> ) |

Symmetry code: (i)  $x, y, z-1$ ; (ii)  $x, y, 1+z$ ; (iii)  $-x, -y, -z$ ; (iv)  $1-x, -y, -z$ ; (v)  $1-x, 1-y, 1-z$ .

2726 reflections obtained of which 2057 with  $I > 2.5 \sigma(I)$  used in the calculations. Structure solved by Patterson and Fourier techniques and refined on  $F$  by full-matrix least-squares procedures. Anisotropic temperature parameters for all non-hydrogen atoms. C(6) has a relatively large anisotropic component perpendicular to the acetate plane, indicating significant motion in that direction. The rigid-group model used in the refinement for the C(4) methyl group resulted in two mutually staggered conformations (58:42%). Reflection 100 was excluded from the refinement and an empirical extinction correction applied:  $F^{\text{corr}} = F_{\text{calc}} \times (1 - 0.0001 \times 0.0049 \times F_{\text{calc}}^2 / \sin \theta)$ . Refinement converged to  $R = 0.037$ ,  $R_w = 0.041$   $\{w^{-1} = [\sigma^2(F) + 0.001F^2] / 0.668\}$ ,  $S = 0.73$ ;  $(\Delta/\sigma)_{\text{max}} = 1.2$ ; residual density  $0.67 \text{ e } \text{Å}^{-3}$  (minimum  $-0.41 \text{ e } \text{Å}^{-3}$ ) in the final difference Fourier map. Scattering factors from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion corrections from Cromer & Liberman (1970). Structure determination carried out using the program *SHELX76* (Sheldrick, 1976) and the *EUCLID* package (Spek, 1982), run on the CDC-CYBER-175 of the Computer Centre of the University of Utrecht.

### Discussion.

Table 1 lists the final atomic parameters.\* Fig. 1 illustrates the asymmetric part of the unit cell with composition  $\text{Ca}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$  along with the adopted numbering scheme. These asymmetric units are linked into infinite multiple O-bridged double-stranded Ca chains that zigzag in the  $a$  direction as shown in Fig. 2. The double-stranded chains are cross-linked in the remaining two directions *via* four different hydrogen bridges. Ca(1) is coordinated by eight O atoms belonging to six acetate ligands. Its coordination can be described as a monocapped pentagonal bipyramid. Ca(2) is coordinated by seven O atoms of four acetate ligands and two water molecules thus forming a pentagonal bipyramid. Relevant data on the geometry are given in Table 2. Acetate group C(5)C(6)O(5)O(6) acts as a monodentate ligand. The

\* Lists of structure factors, anisotropic temperature factors, and bond distances and angles for the H atoms and a more complete drawing of the packing have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38859 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

remaining acetate groups act both as bidentate chelating and as O-bridging ligands, in a manner similar to that found in the structure of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (Harrison & Trotter, 1972).

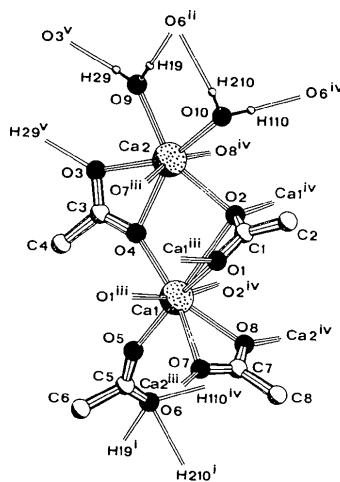


Fig. 1. The asymmetric unit of the structure of  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  together with the adopted numbering scheme and contacts to symmetry-related atoms. Triple lines are used to indicate the Ca coordination whereas double lines represent hydrogen bridges. For the symmetry code see Table 2.

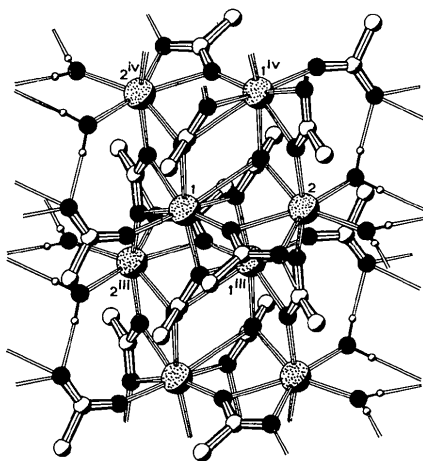


Fig. 2. View of the double-stranded Ca chain running along the  $a$  axis. Ca atoms are indicated by dotted spheres and O atoms by black spheres.

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## Structure of 1,3-(1,1'-Ruthenocenediyl)propane, $C_{13}H_{14}Ru$ , and 1,4-(1,1'-Ruthenocenediyl)butane, $C_{14}H_{16}Ru$

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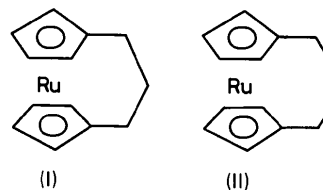
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**Abstract.**  $C_{13}H_{14}Ru$  (I):  $M_r = 271.3$ , monoclinic,  $Pa$ ,  $a = 11.448$  (1),  $b = 7.499$  (1),  $c = 6.273$  (1) Å,  $\beta = 111.30$  (1)°,  $V = 501.7$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.80$ ,  $D_m = 1.80$  (2) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu(\text{Mo } K\alpha) = 1.49$  mm<sup>-1</sup>,  $F(000) = 272$ ,  $T = 295$  (2) K,  $R = 0.016$  for 1389 unique reflections.  $C_{14}H_{16}Ru$  (II):  $M_r = 285.4$ , monoclinic,  $P2_1/c$ ,  $a = 11.997$  (3),  $b = 12.718$  (2),  $c = 7.725$  (2) Å,  $\beta = 107.03$  (2)°,  $V = 1126.9$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.68$ ,  $D_m = 1.66$  (2) Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.33$  mm<sup>-1</sup>,  $F(000) = 576$ ,  $T = 295$  (2) K,  $R = 0.033$  for 2025 unique reflections. The cyclopentadienyl (Cp) rings take the eclipsed conformation and the dihedral angles between them are 14.8 (2) and 1.7 (2)° for (I) and (II), respectively. The C–C–C angles in the carbon chain connecting the two Cp rings are in the range 114.5 (3) to 116.7 (3)°, showing slight strain in this bridge.

**Introduction.** The structures of several ferrocenophanes have been investigated by the X-ray diffraction method (Jones, Marsh & Richards, 1965; Laing & Trueblood, 1965; Cameron & Cordes, 1979). However, no ruthenocenophanes were reported. Recently, the [3](1,1')- and [4](1,1')ruthenocenophanes [(I) and (II), respectively] were synthesized (Kamiyama, Suzuki, Kimura & Kasahara, 1978). The crystal structure

determination of these compounds has been undertaken to reveal the change in the molecular structure caused by introducing a heteroannularly bridged carbon chain into a ruthenocene molecule.



**Experimental.** Experimental conditions are shown in Table 1.  $D_m$  measured by flotation in aqueous solution of zinc iodide; X-ray intensity measurements performed on a Rigaku AFC-5 four-circle diffractometer with  $\text{Mo } K\alpha$  radiation monochromatized by a graphite plate,  $\theta$ - $2\theta$  scan with a scan speed of 2° min<sup>-1</sup> in  $\theta$ . Space group  $Pa$  is derived from  $Pc$  by permutation of the standard  $abc$  to the  $c\bar{b}a$  orientation, general equivalent positions  $x, y, z; \frac{1}{2} + x, \bar{y}, z$ ; the cell edges were labelled so that  $c < a$  following the recommendations of the Commission on Crystallographic Data (Kennard, Speakman & Donnay, 1967). Corrections for Lorentz and polarization applied but not for absorption. Structure of (I) solved by the heavy-atom method, that

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