

Cadmium(II) Maleate Dihydrate (Cc Form)

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Abstract. $\text{Cd}(\text{C}_4\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$, monoclinic, $M_r = 262$, $a = 6.08$ (1), $b = 16.30$ (1), $c = 7.00$ (1) Å, $\beta = 93.8$ (1)°, $V = 692$ Å³, $D_m = 2.50$, $D_c = 2.52$ Mg m⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 0.31$ mm⁻¹, $F(000) = 504$, space group *Cc* (confirmed by intensity statistics and structure determination), crystal size $0.3 \times 0.3 \times 0.3$ mm. The structure was solved by direct and heavy-atom methods and refined by full-matrix least squares to a final $R = 0.025$ for 728 reflexions. The structure contains only one type of Cd atom, in contrast to that of Post & Trotter [*J. Chem. Soc. Dalton Trans.* (1974), pp. 674–678] in space group $P2_1/c$.

Introduction. The structure of cadmium maleate dihydrate in space group $P2_1/c$ has been reported by Post & Trotter (1974), hereafter referred to as PT; we now report the structure of a second polymorph in space group *Cc* which was prepared by dissolving cadmium(II) carbonate in aqueous maleic acid in the molar ratio 1:2 at 293 K, stirring and leaving for 72 h before filtering. Colourless crystals were produced by allowing the filtrate to stand at room temperature for 2 d. The PT crystals were obtained by heating the initial solution and then cooling until the crystals precipitated.

The data were collected on a Hilger & Watts Y290 four-circle diffractometer with Mo $K\alpha$ radiation to $\theta_{\text{max}} = 28^\circ$, using a θ - 2θ scan. 837 unique reflexions were measured, all of which were considered to be observed [$I > 2\sigma(I)$]. The structure was solved using the *MULTAN* system of programs (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined with *SHELX 76* (Sheldrick, 1976). All the heavy atoms were allowed anisotropic temperature factors, and the weights used were $w = 1/[\sigma(I)^2 + 0.001|F_o|^2]$, the R factor being defined as $\sum w^{1/2}||F_o| - |F_c|| / \sum w^{1/2}|F_o|$. The final weighted R for all 837 reflexions was 0.032 (unweighted 0.038). At this stage the reflexions which had been attenuated during data collection were

removed, since there was some doubt about the mechanical operation of the attenuators, and R_w fell to 0.027 (unweighted 0.025) for the remaining 728 reflexions. The deposited structure factor tables† include all the observed reflexions, but the atomic parameters in Table 1 are those obtained in the second refinement. At no stage in the refinement could the H atoms be identified in a difference electron density map. The two highest peaks on the final map were 0.3 e \AA^{-3} , situated 0.8 \AA from the Cd atom.

Discussion. The structure contains only one type of distorted octahedrally coordinated Cd ion, in contrast to PT which contains two chemically distinct Cd ions, one six-coordinate and one eight-coordinate. The coordination distances and angles are given in Table 2. All the O atoms in the structure are coordinated to Cd ions, which are each bonded to two water molecules and four maleate O atoms. The four O atoms in each maleate ion bond to three symmetry-related Cd ions,

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34461 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cd	5000 (–)	3264 (1)	5000 (–)	1.82
C(1)	2080 (9)	4249 (3)	6782 (7)	1.58
C(2)	307 (10)	4694 (3)	7680 (8)	1.74
C(3)	–1341 (9)	4323 (3)	8531 (7)	1.66
C(4)	–1502 (11)	3415 (4)	8815 (9)	1.66
O(1)	3797 (7)	4614 (3)	6347 (6)	2.29
O(2)	1862 (9)	3478 (4)	6445 (8)	1.97
O(3)	–250 (10)	3095 (3)	10173 (8)	1.89
O(4)	–2858 (8)	3000 (3)	7810 (6)	2.13
O(W1)	8346 (14)	3400 (5)	3853 (11)	2.21
O(W2)	–1037 (8)	1288 (3)	6971 (7)	2.53

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but there are no bridging O atoms as in PT. The Cd—O distances vary from 2.224 to 2.521 Å, a much less extreme variation than in PT. The Cd—O(water) distances (2.247 and 2.291 Å) are similar to the equivalent average value in PT (2.28 Å). The bidentate carboxylate-ion group coordinates asymmetrically to the metal.

There are no significant differences between the bond lengths and angles within the maleate ion which are listed in Table 3 and those in PT. As in PT the chain of four C atoms is planar, and the carboxyl groups are rotated with respect to the plane, by 17° for the group C(2), C(1), O(1), O(2) and 79° for the group C(3),

Table 2. Bond distances (Å) and angles (°) involving the Cd atom

Symmetry elements: (I) $1 + x, y, z$; (II) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

Cd—O(1)	2.521 (5)	Cd—O(W1)	2.247 (8)
Cd—O(2)	2.245 (6)	Cd—O(4)(I)	2.326 (4)
Cd—O(3)(II)	2.224 (5)	Cd—O(W2)(II)	2.291 (5)
O(1)—Cd—O(2)	54.5 (2)	O(2)—Cd—O(3)(II)	93.8 (2)
O(1)—Cd—O(3)(II)	145.7 (2)	O(2)—Cd—O(W1)	164.2 (3)
O(1)—Cd—O(W1)	109.8 (2)	O(2)—Cd—O(4)(I)	95.3 (2)
O(1)—Cd—O(4)(I)	90.3 (2)	O(2)—Cd—O(W2)(II)	100.2 (2)
O(1)—Cd—O(W2)(II)	89.9 (2)	O(3)(II)—Cd—O(W1)	100.6 (3)
O(W1)—Cd—O(4)(I)	81.4 (2)	O(3)(II)—Cd—O(4)(I)	78.8 (2)
O(W1)—Cd—O(W2)(II)	80.7 (2)	O(3)(II)—Cd—O(W2)(II)	110.6 (2)
O(4)(I)—Cd—O(W2)(II)	161.1 (2)		

Table 3. Bond distances (Å) and angles (°) in the maleate ion

C(1)—C(2)	1.47 (1)	C(3)—C(4)	1.50 (1)
C(1)—O(1)	1.26 (1)	C(4)—O(4)	1.25 (1)
C(1)—O(2)	1.28 (1)	C(4)—O(3)	1.29 (1)
C(2)—C(3)	1.34 (1)		
C(2)—C(1)—O(1)	121 (1)	C(3)—C(4)—O(4)	121 (1)
C(2)—C(1)—O(2)	119 (1)	C(3)—C(4)—O(3)	117 (1)
O(1)—C(1)—O(2)	120 (1)	O(4)—C(4)—O(3)	122 (1)
C(1)—C(2)—C(3)	124 (1)	C(2)—C(3)—C(4)	124 (1)

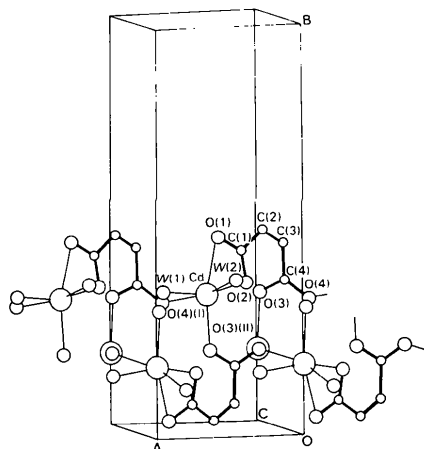


Fig. 1. The arrangement of the structure in the unit cell, showing the coordination around four Cd atoms.

Table 4. Short oxygen—oxygen contacts (Å) and angles (°)

Symmetry elements		(d)	$x - \frac{1}{2}, y - \frac{1}{2}, z$
(a)	$1 + x, y, z$	(e)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
(b)	$1 + x, y, z - 1$	(f)	$x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
(c)	$\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$		
O(W1)—O(2) ^a	2.71 (1)	O(W2)—O(4)	3.07 (1)
O(W1)—O(3) ^b	2.81 (1)	O(W2)—O(1) ^d	2.76 (1)
O(W1)—O(4) ^a	2.98 (1)	O(W2)—O(W1) ^e	2.94 (1)
O(W1)—O(W2) ^c	2.94 (1)	O(W2)—O(3) ^f	2.95 (1)
O(2) ^a —O(W1)—O(3) ^b	110.3 (3)	O(4)—O(W2)—O(1) ^d	156.4 (3)
O(2) ^a —O(W1)—O(4) ^a	67.7 (2)	O(4)—O(W2)—O(W1) ^e	94.9 (2)
O(2) ^a —O(W1)—O(W2) ^c	160.5 (4)	O(4)—O(W2)—O(3) ^f	57.3 (2)
O(3) ^b —O(W1)—O(4) ^a	156.9 (4)	O(1) ^d —O(W2)—O(W1) ^e	105.3 (2)
O(3) ^b —O(W1)—O(W2) ^c	86.6 (3)	O(1) ^d —O(W2)—O(3) ^f	104.3 (2)
O(4) ^a —O(W1)—O(W2) ^c	100.5 (3)	O(W1) ^e —O(W2)—O(3) ^f	150.1 (3)

C(4), O(3), O(4). This asymmetry is similar to that in PT [angles in maleate ion (1): 18 and 84°; in maleate ion (2): 16 and 67°] and in tin(II) maleate monohydrate (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977) where the corresponding angles are 4 and 88°, but in contrast to that in copper(II) maleate hydrate (Prout, Carruthers & Rossotti, 1971) in which both angles are 46°.

Since it was not possible to locate the H atoms in the crystal, there is some doubt about the hydrogen bonding. The short oxygen—oxygen contacts are listed in Table 4, and the arrangement of the structure in the cell is shown in Fig. 1. Consideration of the angles made by the contacts about the water molecules suggests that O(W1) may be hydrogen bonded to O(2) and O(3), and that O(W2) may be hydrogen bonded to O(1) and O(3), although other hydrogen-bonding schemes cannot be ruled out.

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References

- DEWAN, J. C., SILVER, J., ANDREWS, R. H., DONALDSON, J. D. & LAUGHLIN, D. R. (1977). *J. Chem. Soc. Dalton Trans.* pp. 368–371.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- POST, M. L. & TROTTER, J. (1974). *J. Chem. Soc. Dalton Trans.* pp. 674–678.
- PROUT, C. K., CARRUTHERS, J. R. & ROSSOTTI, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3342–3349.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.