Crystal Structure of Polymeric Cadmium(II) Malonate Monohydrate

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Crystals of the title compound are trigonal (based on hexagonal axes), space group $R\bar{3}$, $a = b = 17{\cdot}216(9)$, $c = 10{\cdot}894(4)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $Z = 18$. The structure was determined from *X*-ray diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares calculations to *R* 0·048 for 1071 observed reflections. Each malonate ligand chelates three symmetry-related cadmium atoms with two of the oxygen atoms also in bridging positions. The lattice formed is polymeric and further strengthened by hydrogen bonding *via* a co-ordinated water molecule. The cadium atom is seven-co-ordinate in nearly pentagonal bipyramidal geometry with Cd–O 2·272(7)—2·501(7) Å. The mode of chelation exhibited by the malonate ion has not previously been reported.

CADMIUM(II) malonate forms at least two stable crystalline hydrates, both of which are sparingly soluble in water and most other common solvents. This is in marked contrast to the Cd complexes of carboxylates such as acetic,[1] cyanoacetic,[2] maleic,[3] and formic [4] acids which exhibit very high aqueous solubility despite the presence of polymerisation. From *X*-ray photographic studies, both the hydrates appeared structurally related and cadmium(II) malonate monohydrate was chosen as the subject for full *X*-ray structural analysis to investigate the mode of co-ordination and suspected polymerisation in the crystal lattice.

EXPERIMENTAL

Cadmium(II) malonate was prepared by dissolving finely divided cadmium(II) carbonate in a hot aqueous solution of malonic acid. Over a period of 5 weeks, the filtrate yielded a small crop of transparent, poorly formed, crystals consisting of both the mono- and di-hydrates. A choice of space groups and preliminary unit-cell dimensions for both hydrates were determined from precession and Weissenberg photographs. Accurate cell parameters for the monohydrate were obtained later from a least-squares treatment of the 2θ values of 13 reflections, measured on a General Electric XRD 6 diffractometer.

Crystal Data, Based on Hexagonal Axes.—(i) Cadmium(II) malonate dihydrate, $C_3H_6CdO_6$, $M = 250{\cdot}48$, Trigonal, $a = b = 17{\cdot}13(7)$, $c = 12{\cdot}48(4)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $U = 3171{\cdot}5$ Å^3, $Z = 18$. Space group $R\bar{3}$ or $R3$ from systematic absences: $-h + k + l \neq 3n$.

(ii) Cadmium(II) malonate monohydrate, $C_3H_4CdO_5$, $M = 232{\cdot}46$, Trigonal, $a = b = 17{\cdot}216(9)$, $c = 10{\cdot}894(4)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $U = 2796{\cdot}3$ Å^3, $Z = 18$, $F(000) = 1980$, Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 34{\cdot}4$ cm^{-1}. Space group $R\bar{3}$ or $R3$ from systematic absences: $-h + k + l \neq 3n$.

For data collection, a crystal of the monohydrate shaped as an approximately rectangular prism with the *c* direction elongated, and size *ca*. 0·3 × 0·3 × 0·5 mm, was mounted with the *c* axis coincident with the ϕ axis of a Datex-automated General Electric XRD 6 diffractometer. All reflections with $2\theta(\text{Mo-}K_\alpha) \leqslant 55°$ were measured by use of a θ—2θ scan at 2° min^{-1} in 2θ, and of a total 1424 independent observations, 353 had intensities $< 3\sigma(I)$ above background [$\sigma(I)$ is defined by: $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, where S = scan count and B = background], and were treated as unobserved. A check and scaling reflection was monitored every 30 reflections, its value changing by $< \pm 4\%$ throughout data collection. Lorentz and polarisation corrections were applied and relative structure factors derived. No absorption correction was made.

Structure Solution and Refinement.—A statistical treatment [5] of the $|E|$ values indicated the centrosymmetric space group, $R\bar{3}$, to be correct and all subsequent steps in the determination supported this choice. The position of the cadmium atom was found from a Patterson synthesis, a structure-factor calculation yielding *R* 0·22. The positions of all the remaining non-hydrogen atoms were found from two subsequent Fourier syntheses, and after two cycles of isotropic refinement, *R* was 0·081. At this stage the two methylene and two water molecule hydrogen atoms were located from a difference-Fourier synthesis, and they were included in the following structure factor calculations (B_{iso} 5·0 Å^2), but were not refined. Refinement was continued with anisotropic thermal parameters, the scattering factor

TABLE 1

Final positional parameters (× 10^4) with standard deviations in parentheses

Atom	*x*	*y*	*z*
Cd	2491·1(4)	2661·8(4)	251·7(5)
O(1)	857(4)	2142(5)	475(6)
O(2)	1610(4)	2001(5)	1984(6)
O(3)	−546(4)	2435(4)	1781(5)
O(4)	−141(5)	2510(5)	3683(6)
O(5)	2825(5)	4084(5)	703(6)
C(1)	893(5)	1910(5)	1567(7)
C(2)	59(6)	1504(6)	2372(8)
C(3)	−225(6)	2189(6)	2639(8)
H(1)	190	1290	3180
H(2)	−460	970	1920
H(3)	3010	4410	−80
H(4)	3240	4260	1280

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of the cadmium atom being corrected for the real and imaginary components of anomalous dispersion, and after four cycles, convergence was reached at R 0·048 with no shift $>0{\cdot}05\sigma$ in the final cycle. A weighting scheme of the form $w = 1{\cdot}0$ if $|F_0| < F^*$; $w^{\frac{1}{2}} = F^*/|F_0|$ if $|F_0| \geqslant F^*$ with $F^* = 130{\cdot}0$ was employed in the final stages, the weighted R being 0·062. Final positional and thermal parameters are presented in Tables 1 and 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21054 (14 pp., 1 microfiche).†

TABLE 2

Final anisotropic thermal parameters * (Å^2 × 10^3) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	34·6(4)	34·6(4)	25·5(3)	15·9(3)	0·6(2)	−1·7(2)
O(1)	43(4)	49(4)	30(3)	26(3)	6(3)	7(3)
O(2)	37(3)	58(4)	31(3)	27(3)	−1(3)	4(3)
O(3)	27(3)	43(4)	30(3)	13(3)	2(2)	−1(3)
O(4)	57(4)	56(4)	27(3)	32(4)	−3(3)	−7(3)
O(5)	48(4)	41(4)	33(3)	21(3)	0(3)	0(3)
C(1)	30(4)	28(4)	26(4)	15(3)	0(3)	−3(3)
C(2)	42(5)	39(5)	31(4)	23(4)	10(4)	11(4)
C(3)	32(4)	40(5)	27(4)	19(4)	4(3)	−1(3)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

DISCUSSION

Structural details are shown in Figure 1 and a clearer view of the co-ordination geometry about the Cd atom is shown in Figure 2, which contains only Cd and oxygen atoms for clarity. Tables 3 and 4 show bond lengths and angles, respectively, while principal least-square mean planes are presented in Table 5.

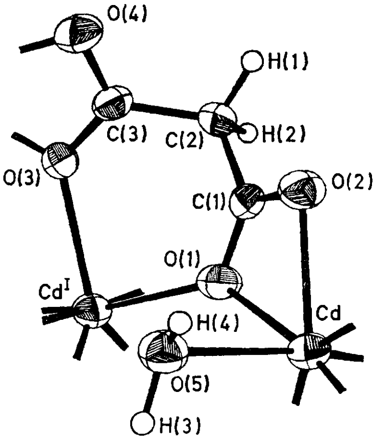

FIGURE 1 Perspective view with all non-hydrogen atoms represented by 50% probability thermal ellipsoids

The complexity of the arrangement is apparent from Figure 1 while the mode of extension into a three-dimensional polymer is more readily seen in the stereoscopic packing diagram (Figure 3). Each malonate ligand is involved in chelating three symmetry-related Cd atoms, two of which are present in Figure 1, the third metal atom, Cd$^{\mathrm{III}}$, being chelated by atoms O(3) and O(4) and lying in symmetry position $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$. The atoms O(1) and O(3) are also in bridging

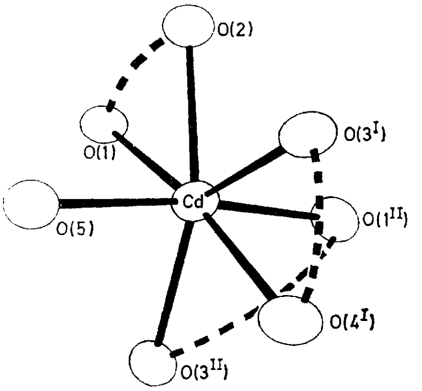

FIGURE 2 Perspective view of the co-ordination around Cd. Broken lines connect pairs of chelating atoms

TABLE 3

Bond distances (Å) with standard deviations in parentheses

Cd–O(1)	2·501(7)	C(1)–C(2)	1·521(11)
Cd–O(2)	2·330(6)	C(3)–O(3)	1·260(10)
Cd$^{\mathrm{I}}$–O(1)	2·277(7)	C(3)–O(4)	2·241(11)
Cd$^{\mathrm{I}}$–O(3)	2·296(6)	C(3)–C(2)	1·516(12)
Cd–O(3$^{\mathrm{I}}$)	2·417(6)	O(5)–H(3)	0·98
Cd–O(4$^{\mathrm{I}}$)	2·398(7)	O(5)–H(4)	0·89
Cd–O(5)	2·272(7)	C(2)–H(1)	1·02
C(1)–O(1)	1·266(10)	C(2)–H(2)	1·03
C(1)–O(2)	1·250(10)		

Cd$^{\mathrm{I}}$ is at $x - y, x, -z$; O(3$^{\mathrm{I}}$) and O(4$^{\mathrm{I}}$) are at $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$.

TABLE 4

Bond angles (°) with standard deviations in parentheses

O(1)–Cd–O(2)	53·5(2)	O(3$^{\mathrm{II}}$)–Cd–O(5)	88·2(2)
O(1)–Cd–O(3$^{\mathrm{I}}$)	136·9(2)	O(1$^{\mathrm{II}}$)–Cd–O(5)	172·1(2)
O(1)–Cd–O(4$^{\mathrm{I}}$)	169·6(2)	Cd–O(1)–Cd$^{\mathrm{I}}$	139·0(3)
O(1)–Cd–O(3$^{\mathrm{II}}$)	90·3(2)	Cd–O(1)–C(1)	88·9(5)
O(1)–Cd–O(1$^{\mathrm{II}}$)	89·8(3)	Cd$^{\mathrm{I}}$–O(1)–C(1)	125·2(5)
O(1)–Cd–O(5)	89·9(2)	Cd–O(2)–C(1)	97·4(5)
O(2)–Cd–O(3$^{\mathrm{I}}$)	83·5(2)	O(1)–C(1)–O(2)	120·2(8)
O(2)–Cd–O(4$^{\mathrm{I}}$)	136·7(2)	O(1)–C(1)–C(2)	120·2(7)
O(2)–Cd–O(3$^{\mathrm{II}}$)	143·4(2)	O(2)–C(1)–C(2)	119·6(7)
O(2)–Cd–O(1$^{\mathrm{II}}$)	90·3(2)	C(1)–C(2)–C(3)	110·6(7)
O(2)–Cd–O(5)	95·9(2)	O(3)–C(3)–O(4)	120·2(8)
O(3$^{\mathrm{I}}$)–Cd–O(4$^{\mathrm{I}}$)	53·5(2)	O(3)–C(3)–C(2)	119·1(7)
O(3$^{\mathrm{I}}$)–Cd–O(3$^{\mathrm{II}}$)	132·9(2)	O(4)–C(3)–C(2)	120·7(8)
O(3$^{\mathrm{I}}$)–Cd–O(1$^{\mathrm{III}}$)	93·8(2)	Cd$^{\mathrm{I}}$–O(3)–Cd$^{\mathrm{III}}$	131·6(3)
O(3$^{\mathrm{I}}$)–Cd–O(5)	91·8(2)	Cd$^{\mathrm{I}}$–O(3)–C(3)	124·6(5)
O(4$^{\mathrm{I}}$)–Cd–O(3$^{\mathrm{II}}$)	79·3(2)	Cd$^{\mathrm{III}}$–O(3)–C(3)	92·4(5)
O(4$^{\mathrm{I}}$)–Cd–O(1$^{\mathrm{III}}$)	88·3(3)	Cd$^{\mathrm{III}}$–O(4)–C(3)	93·8(6)
O(4$^{\mathrm{I}}$)–Cd–O(5)	90·6(3)	H(1)–C(2)–H(2)	109·9
O(3$^{\mathrm{II}}$)–Cd–O(1$^{\mathrm{II}}$)	83·9(2)	H(3)–O(5)–H(4)	116·3

O(1$^{\mathrm{II}}$) and O(3$^{\mathrm{II}}$) are at $y, y - x, -z$.

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

positions to make each of the malonate carboxy-groups terdentate. In this manner, one six-membered [Cd$^{\mathrm{I}}$,O(1),C(1),C(2),C(3),O(3)] and two four-membered [Cd,O(1),C(1),O(2) and Cd$^{\mathrm{III}}$,O(3),C(3),O(4)] chelate rings are formed in the structure. The co-ordination sphere about Cd is completed with one water molecule at O(5) to give a co-ordination number of seven, and a polyhedron with geometry close to that of a pentagonal bipyramid (Figure 2). Atoms Cd,O(1),O(2),O(3$^{\mathrm{I}}$),O(4$^{\mathrm{I}}$),O(3$^{\mathrm{II}}$) lie close to a plane, from which the maximum deviation of atoms concerned is 0·085 Å, while atoms O(5) and O(1$^{\mathrm{II}}$) [O(5)–Cd–O(1$^{\mathrm{II}}$) 172·1°] form the pyramidal apices at very similar distances from Cd. The regularity of the arrangement is necessarily broken by the chelation angles subtended at Cd by the rigid four-membered chelate rings (53·5°), the regular pentagon value being 72°. Seven-co-ordinate Cd has previously been reported,[1,6] and in one case a geometry close to that reported here has been found.

TABLE 5

Equations of some least-square mean planes based on crystallographic co-ordinates x,y,z, with distances (Å) of atoms from the planes in square brackets

Plane (1): Cd, O(1), O(2), O(3$^{\mathrm{I}}$), O(4$^{\mathrm{I}}$), O(3$^{\mathrm{II}}$)

$$-4{\cdot}843x + 16{\cdot}131y + 2{\cdot}990z = 3{\cdot}126$$

[Cd 0·037, O(1) 0·056, O(2) −0·085, O(3$^{\mathrm{I}}$) 0·048, O(4$^{\mathrm{I}}$) −0·027, O(3$^{\mathrm{II}}$) −0·029]

Plane (2): O(1), O(2), C(1), C(2)

$$-4{\cdot}151x + 15{\cdot}710y + 3{\cdot}539z = 3{\cdot}179$$

[O(1) −0·002, O(2) −0·002, C(1) 0·005, C(2) −0·002, Cd 0·058]

Plane (3): O(3), O(4), C(2), C(3)

$$10{\cdot}944x + 5{\cdot}496y - 2{\cdot}547z = 0{\cdot}287$$

[O(3) 0·001, O(4) 0·001, C(2) 0·001, C(3) −0·002, Cd$^{\mathrm{III}}$ 0·119]

Plane (4): O(1), O(3), C(1), C(3)

$$4{\cdot}588x + 11{\cdot}799y + 2{\cdot}053z = 3{\cdot}003$$

[O(1) 0·015, O(3) −0·015, C(1) −0·018, C(3) 0·018, C(2) −0·715, Cd$^{\mathrm{I}}$ 0·066]

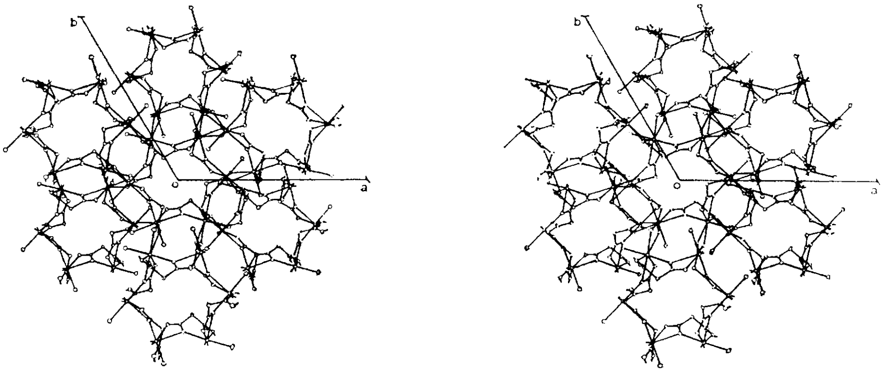

FIGURE 3 Stereoscopic view of the polymeric lattice looking down the c axis

One of the more obvious aspects of the polymeric structure, and clearly visible in Figure 3, is the twelve-membered star-shaped rings which have $\bar{3}$ symmetry. These are formed specifically by the atom types Cd and bridging O(1) in alternation. The distance across the ring between diametrically opposite oxygen atoms is 6·51 Å, this hole being large enough to contain a solvent molecule. No electron density was present in this region, however, presumably the integrity of the surrounding lattice being a sufficient barrier to penetration even at the crystallisation stage. The deviations of Cd and O(1) atoms from the ring mean plane, which is parallel to ab, are ±0·275 and ±0·518 Å, respectively. The polymer is further extended in two ways: first by chelation linkages between cadmium atoms in adjacent star-shaped rings *via* the malonate carbon chain (*i.e.* –Cd–malonate–Cd$^{\mathrm{III}}$–), to form spirals, the axes of which are parallel to the crystallographic c-axis, and secondly by formation of eight-membered loops in general orientation consisting of two –Cd–O(1)–Cd–O(3)– residues. The water hydrogen atoms H(3) and H(4) are both involved in hydrogen bonds with malonate, non-bridging oxygen atoms on adjacent rings (Table 6), and add further to the strength of the lattice. The extremely low solubility of the compound, particularly with respect to other cadmium carboxylates, is probably best explained in terms of the highly efficient and intimate mode of polymerisation of the crystalline lattice.

The Cd–O distances vary from 2·272 to 2·501 Å, a range consistent with values found in other work,[1-4] the large variation within one compound not being unusual. Also as found previously,[1,3,7] the bridging oxygen atoms are not equally shared between cadmium atoms, the bonds in this case being shorter on the six-membered chelate ring side. This should not necessarily

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[7] F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *J.C.S. Dalton*, 1973, 248.

be correlated with the efficiency of formation of the six-membered over the four-membered ring, since previous examples have shown a similar trend even when no extra chelate ring has been created.[1,3] The conformation of the six-membered ring can best be described as a chair considerably flattened at one end, the Cd^{I} and C(2) atoms lying 0·066 and −0·715 Å, respectively, from the O(1),O(3),C(1),C(3) mean plane. In the ions [Co(malonate)$_2$(ethylenediamine)]$^-$ and [Cr(malonate)$_3$]$^{3-}$, boat and flattened-boat conformations, respectively, have been noted[8] in corresponding rings. In these cases, however, no other chelation involving malonate ligands was occurring in the complex. In contrast, the two four-membered chelate rings in the present compound are close to planar with the metal atoms lying *ca.* 0·06 and 0·12 Å from the respective mean planes of the acetato-moieties. The ligand bites O(1) · · · O(2) and O(3) · · · O(4) are 2·181(9) and 2·169(9) Å, while O(1) · · · O(3) is 3·055(9) Å. Within the carboxy-groups, variation in the bites is severely restricted by trigonal bonding geometry at the carbon atom and the values here are very similar to those found even in unidentate[9,10] and free[11] carboxy-groups. The distance O(1) · · · O(3) is not limited in this manner and is mainly dependent upon the degree of rotation about the single bonds C(1)–C(2) and C(2)–C(3) which can, theoretically, assume a variety of values. The torsion angles O(1)–C(1)–C(2)–C(3) and O(3)–C(3)–C(2)–C(1) are −66·1 and 70·0°, these similar but opposite values conferring upon the malonate ligand a pseudo-mirror plane coincident with H(1)–C(2)–H(2). In malonic acid itself,[12] and some of its α-derivatives,[13-17] these torsion angles assume quite different values, but in each case they yield distances corresponding to O(1) · · · O(3), which are close to 3 Å. In the present complex, other bond lengths and angles concerning the malonate ligand are as expected.

TABLE 6

Hydrogen-bond distances (Å) and angles (°)

Bond	Symmetry relation of · · · O	O · · · O	O–H · · · O
O(5)–H(3) · · · O(2)	$\frac{1}{3} - x + y, \frac{2}{3} - x, -\frac{1}{3} + z$	2·758(9)	160·4
O(5)–H(4) · · · O(4)	$\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$	2·703(10)	145·2

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