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# The Structure of Monoclinic Cadmium Oxydiacetate Trihydrate

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The structure of monoclinic $CdO(CH_2COO)_2.3H_2O$ has been determined and refined to $R = 0.069$. The crystals are monoclinic, space group $P2_1/c$, with $a = 6.3848 (7)$, $b = 10.2093 (9)$, $c = 14.0470 (16)$ Å, $\beta = 101.753 (10)°$, $Z = 4$. The crystal structure consists of discrete units of composition $2CdO(CH_2COO)_2.6H_2O$ held together by hydrogen bonds. In each unit, the two Cd atoms are bridged by two O atoms, one from each oxydiacetate ion, the remaining coordination sites about the seven-coordinate Cd atom being occupied by two more O atoms from one of the bridging oxydiacetate ions, giving a tridentate chelate, and by three water O atoms. The coordination polyhedron is a pentagonal bipyramid and within each unit the two bipyramids have one equatorial edge in common. The Cd—O distances range from 2.236 (7) to 2.492 (8) Å; the Cd—Cd distance in a unit is 3.968 (1) Å. The non-hydrogen atoms are coplanar in each oxydiacetate half with an angle of 8° between the planes.

## Introduction

In this paper the structure of CDOXY II, one of the three Cd oxydiacetate hydrates reported by Boman (1974), is described in detail. Descriptions of the other two, CDOXY III and CDOXY I, have already been given (Boman, 1977a,b). A brief comparison between the three structures, as well as their relations to some similar Cd structures, is included.

## Crystal data

Cadmium oxydiacetate trihydrate or di-$\mu$-oxy-diacetato-bis(triaquacadmium), $CdC_4H_{10}O_8$ (CDOXY II); FW 298.5 g mol$^{-1}$; monoclinic, space group $P2_1/c$; $a = 6.3848$ (7), $b = 10.2093$ (9), $c = 14.0470$ (16) Å, $\beta = 101.753$ (10)°; $V = 896.4$ Å$^3$; $Z = 4$; $\mu(Cu K\alpha) = 204.8$ cm$^{-1}$; $D_m = 2.18$, $D_x = 2.21$ g cm$^{-3}$.

## Experimental

The colourless crystals were prepared as described earlier (Boman, 1974). Elemental analyses and complexometric titration of Cd gave values in good agreement with the composition given by the formula. The density was obtained from the loss of weight in $CCl_4$.

The monoclinic symmetry was deduced from Weissenberg photographs and the systematic absences were those characteristic of space group $P2_1/c$. The preliminary cell dimensions obtained from Weissenberg photographs were refined by least squares applied to powder data from a Guinier–Hägg camera of radius 5·00 cm (Cu $K\alpha_1$ radiation, $\lambda = 1·54051$ Å) with Al (cubic, $a = 4·04934$ Å, 22°C) as internal standard. A crystal, 0·05 × 0·14 × 9·15 mm, mounted along b was used for data collection on an automatic diffractometer of type CAD-4. Intensities were recorded with Cu $K\alpha$ radiation monochromatized by reflexion in a graphite crystal at a take-off angle of 5°. The $\omega$–2$\theta$ technique was used with a scan interval $\Delta\omega$  0·70 + 0·40 tan $\theta$. The background was measured before and after each reflexion. All 1794 independent reflexions in the interval 5° < $\theta$ < 70° were measured, but 349 reflexions with $I < 3\sigma_c(I)$ were rejected in the subsequent calculations. A fast pre-scan was used to determine the scan speed at which a predetermined minimum of counts (3000) were received by the detector, no reflexion, however, being measured for more than 180 s. The values of $\sigma_c(I)$ were based on counting statistics. The reflexions 015, 221 and 211 were chosen as standards and the intensity of each was measured every hour. The fluctuations were random and less than 10%. The values of $I$ and $\sigma_c(I)$ were corrected for absorption, polarization and the Lorentz effect. The transmission factors varied from 0·231 to 0·462.

## Structure determination and refinement

The Cd atom was located in a Patterson synthesis. The remaining non-hydrogen atoms were found in subsequent difference syntheses. The H atoms were not found.

Full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$ was performed with $w = 1/(\sigma_c^2 + a|F_o|^2)$, where $a$ was chosen to make the average values as equal as possible in the different $|F_o|$ and sin $\theta$ intervals. In the last cycles the value of $a$ was 0·0025. The convergence was checked by $R = \Sigma \||F_o| - |F_c\|/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. In the last cycles anisotropic temperature factors were used for all 13 atoms making a total of 118 parameters. Scattering factors for Cd were those given by Cromer & Waber (1965) and for O and C by Hanson, Herman, Lea & Skillman (1964), in all cases for the neutral atoms.

The final value of $R$ was 0·069 and $R_w = 0·099$, with

shifts less than 1% of the estimated standard deviations. $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where $m$ is the number of observations and $n$ the number of parameters, was 2·00. A difference map calculated at this stage contained a pit 2·5 e Å$^{-3}$ deep at the Cd position but also a peak of about 3·5 e Å$^{-3}$ at 0,$\frac{1}{2}$,0, a centre of symmetry. This could indicate the presence of a disordered water molecule in the structure. A refinement with one O atom in this position gave $B = 11·5$ Å$^2$ for this atom and $R = 0·064$, and with one half of an atom the values were 6·3 Å$^2$ and 0·067. In the latter case anisotropic refinement resulted in a negative $B$ value. The changes in the parameters for the other atoms were not significant and the distances and angles calculated with the new values agreed within one standard deviation with the old ones. In a final difference map the peak was absent but the pit at the Cd position was now deeper, 3·4 e Å$^{-3}$. It thus seems hard to decide whether a disordered water molecule occurs in the structure or not, and so it was neglected in the following calculations.

The atomic coordinates are shown in Table 1 and r.m.s. components along the principal axes of thermal

Table 1. *Atomic coordinates with standard deviations* ($\times 10^4$) *and isotropic temperature factors*

|      | $x$       | $y$        | $z$        | $B$ (Å$^2$) |
|------|-----------|------------|------------|-------------|
| Cd   | 5578 (1)  | 1678 (1)   | 718 (1)    | 2·6         |
| O(1) | 7531 (12) | 855 (7)    | 2202 (5)   | 2·9         |
| O(2) | 6991 (15) | 3344 (7)   | 1819 (6)   | 3·8         |
| O(3) | 8292 (11) | 3928 (8)   | 3368 (5)   | 3·4         |
| O(4) | 6078 (11) | −743 (8)   | 770 (5)    | 3·1         |
| O(5) | 6646 (12) | −2485 (7)  | 1722 (5)   | 3·5         |
| O(6) | 8623 (12) | 1942 (9)   | 186 (6)    | 3·7         |
| O(7) | 3987 (15) | 3644 (10)  | −18 (7)    | 5·0         |
| O(8) | 2664 (10) | 1370 (7)   | 1440 (6)   | 3·0         |
| C(1) | 8117 (17) | 1728 (10)  | 3012 (8)   | 3·1         |
| C(2) | 7758 (15) | 3066 (9)   | 2692 (7)   | 2·8         |
| C(3) | 7408 (16) | −443 (9)   | 2460 (8)   | 3·1         |
| C(4) | 6653 (14) | −1282 (10) | 1573 (7)   | 2·6         |

Table 2. *The r.m.s. components,* $R_i$ ($\times 10^3$ Å), *of thermal displacement along the ellipsoid axes*

|      | $R_1$ | $R_2$ | $R_3$ |
|------|-------|-------|-------|
| Cd   | 229   | 148   | 177   |
| O(1) | 236   | 142   | 210   |
| O(2) | 266   | 175   | 229   |
| O(3) | 235   | 176   | 218   |
| O(4) | 234   | 159   | 210   |
| O(5) | 231   | 188   | 217   |
| O(6) | 300   | 176   | 190   |
| O(7) | 303   | 205   | 260   |
| O(8) | 236   | 163   | 194   |
| C(1) | 233   | 159   | 212   |
| C(2) | 223   | 149   | 195   |
| C(3) | 222   | 176   | 196   |
| C(4) | 235   | 150   | 174   |

ellipsoids are given in Table 2.* The computations were performed on the Univac 1108 in Lund, Sweden (Oskarsson, 1973).

## Description of the structure

The crystal structure, Fig. 1, is built up of discrete units of composition $2CdO(CH_2COO)_2.6H_2O$ held together by hydrogen bonds in a three-dimensional network. Fig. 2 shows the main part of the discrete unit as well as the coordination about Cd, which is sevenfold. The coordination polyhedron is a pentagonal bipyramid with Cd—O distances from 2·236 (7) to 2·492 (8) Å. Coordination distances and other relevant distances and angles in the pentagonal bipyramid are given in Table 3. The first five Cd—O distances are those to the O atoms in the pentagon. The apices are formed by two water oxygens, O(6) and O(8).

The discrete unit consists of two pentagonal bipyramids with one equatorial edge in common and a centre of symmetry on this edge. Except for the apical O atoms the non-hydrogen atoms in the unit are nearly coplanar and lie in a plane parallel to $(10\bar{1})$. Deviations from the least-squares plane through the five equatorial O atoms are in Table 4. The Cd—Cd distance is

3·968 (1) Å in the unit. The Cd atom coordinates three water molecules and two oxydiacetate ions. One water oxygen, O(7), forms one vertex of the pentagon and the other two, O(6) and O(8), form the apices. One oxydiacetate ion is tridentate through O(1), O(2) and O(4) and the other monodentate through O(4'). The bridging between the two Cd atoms in a unit occurs via O(4) and O(4$^i$).

Table 3. *Interatomic distances (Å) and angles (°) in the coordination polyhedron*

The superscripts indicate transformations applied to the coordinates given in Table 1: (i) $1 - x, -y, -z$.

| | | | |
|---|---|---|---|
| Cd—O(2) | 2·352 (8) | O(2)—Cd—O(1) | 67·2 (3) |
| Cd—O(1) | 2·356 (7) | O(1)—Cd—O(4) | 65·1 (2) |
| Cd—O(4) | 2·492 (8) | O(4)—Cd—O(4$^i$) | 69·8 (3) |
| Cd—O(4$^i$) | 2·345 (7) | O(4$^i$)—Cd—O(7) | 83·2 (3) |
| Cd—O(7) | 2·387 (10) | O(7)—Cd—O(2) | 75·5 (3) |
| Cd—O(6) | 2·236 (7) | O(6)—Cd—O(8) | 173·6 (3) |
| Cd—O(8) | 2·315 (7) | | |
| O(2)—O(1) | 2·606 (10) | O(7)—O(2)—O(1) | 108·8 (4) |
| O(1)—O(4) | 2·609 (10) | O(2)—O(1)—O(4) | 116·1 (4) |
| O(4)—O(4$^i$) | 2·768 (14) | O(1)—O(4)—O(4$^i$) | 107·6 (4) |
| O(4$^i$)—O(7) | 3·142 (13) | O(4)—O(4$^i$)—O(7) | 106·5 (4) |
| O(7)—O(2) | 2·901 (13) | O(4$^i$)—O(7)—O(2) | 99·2 (4) |
| O(6)—O(2) | 3·062 (12) | O(8)—O(2) | 3·373 (11) |
| O(6)—O(1) | 3·247 (11) | O(8)—O(1) | 3·118 (10) |
| O(6)—O(4) | 3·372 (12) | O(8)—O(4) | 3·336 (10) |
| O(6)—O(4$^i$) | 3·267 (10) | O(8)—O(4$^i$) | 3·422 (10) |
| O(6)—O(7) | 3·394 (12) | O(8)—O(7) | 3·317 (12) |

* A list of structure factors and anisotropic thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32285 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



Fig. 1. A stereoscopic view of the structure of monoclinic cadmium oxydiacetate trihydrate with the hydrogen bonds marked by thin lines. The $a$ axis is pointing into the paper, $b$ upwards and $c$ to the right.
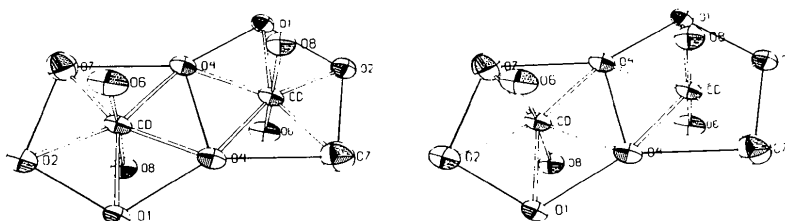


Fig. 2. Two coordination polyhedra sharing an edge. The pentagons are indicated. In Figs. 2 and 3 thermal ellipsoids were used.

Table 5 lists interatomic distances, angles, and dihedral angles for the oxydiacetate ion, shown in Fig. 3. It is almost planar in this structure; the deviations from planarity in the ligand-halves are given in Table 6.

The H atoms could not be located but the hydrogen-

**Table 4.** *Deviations (Å) from the least-squares plane through the pentagon*

Atoms defining plane: O(2), O(1), O(4), O(4$^i$), O(7).

| | | | |
|---|---|---|---|
| O(2) | 0·155 | O(7) | −0·138 |
| O(1) | −0·101 | Cd | 0·004 |
| O(4) | −0·009 | O(6) | 2·237 |
| O(4$^i$) | 0·093 | O(8) | −2·306 |

**Table 5.** *Interatomic distances (Å) and angles (°) for the oxydiacetate ion*

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·433 (13) | C(1)–O(1)–C(3) | 114·1 (8) |
| O(1)–C(3) | 1·380 (12) | O(1)–C(1)–C(2) | 110·0 (9) |
| C(1)–C(2) | 1·442 (14) | O(1)–C(3)–C(4) | 110·8 (8) |
| C(3)–C(4) | 1·508 (14) | C(1)–C(2)–O(2) | 121·6 (8) |
| C(2)–O(2) | 1·256 (13) | C(1)–C(2)–O(3) | 114·6 (9) |
| C(2)–O(3) | 1·289 (12) | O(2)–C(2)–O(3) | 123·8 (9) |
| C(4)–O(4) | 1·241 (12) | C(3)–C(4)–O(4) | 119·0 (9) |
| C(4)–O(5) | 1·246 (13) | C(3)–C(4)–O(5) | 115·7 (9) |
| O(2)–O(3) | 2·245 (11) | O(4)–C(4)–O(5) | 125·4 (9) |
| O(4)–O(5) | 2·210 (11) | | |
| O(1)–O(2) | 2·606 (10) | | |
| O(1)–O(4) | 2·609 (10) | | |
| O(2)–O(4) | 4·424 (11) | | |

Dihedral angles

| | |
|---|---|
| O(1)–C(1)–C(2)–O(2) | 1·4 |
| O(1)–C(1)–C(2)–O(3) | −178·3 |
| O(1)–C(3)–C(4)–O(4) | 6·0 |
| O(1)–C(3)–C(4)–O(5) | −174·7 |

**Table 6.** *Deviations (Å) from the least-squares planes through the independent halves in the oxydiacetate ion*

Atoms defining plane: I O(1), C(1), C(2), O(2), O(3); II O(1), C(3), C(4), O(4), O(5). The angle between the planes is 8°.

| | I | | II |
|---|---|---|---|
| O(1) | 0·011 | O(1) | 0·038 |
| C(1) | −0·014 | C(3) | −0·047 |
| C(2) | −0·004 | C(4) | −0·004 |
| O(2) | −0·004 | O(4) | −0·016 |
| O(3) | 0·010 | O(5) | 0·029 |
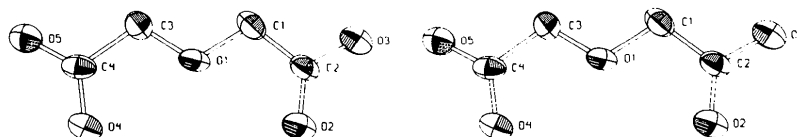
**Table 7.** *Hydrogen-bond distances (Å)*

| | |
|---|---|
| O(6)–H···O(3) | 2·671 (11) |
| O(6)–H···O(8) | 2·872 (10) |
| O(7)–H···O(5) | 2·626 (12) |
| O(8)–H···O(3) | 2·594 (10) |
| O(8)–H···O(5) | 2·787 (11) |
| O(8)···H–O(6) | 2·872 (10) |

bond system could be deduced by geometrical considerations. Relevant O–O distances are given in Table 7. All water H atoms have been assigned to definite water O atoms, but one of the H atoms on O(7) does not take part in the hydrogen-bond system. The two O(7) atoms in a discrete unit have, however, van der Waals contact with the centrosymmetrically related O(7) atoms in adjacent units along **b**, the O(7)–O(7) distance being 3·052 (20) Å. Further, each unit is hydrogen-bonded to six other units through the four apical O atoms. On each side of the unit O(6) and O(8) are bonded to the same O(3) in one unit, and to O(8) and O(6) respectively in a second, and finally O(8) is bonded to an O(5) in a third unit. Within each unit there are two O(7)–H···O(5) intramolecular hydrogen bonds.

In the structure there is room for a water molecule at 0,½,0, but a water molecule at this site does not fit in with the space group. The nearest O atom would be 2·937 (9) Å and the next nearest 3·238 (9) Å away. As the closest Cd atom would be more than 4·5 Å away the coordination would not be influenced.

## Discussion

With this paper the description of the Cd oxydiacetate structures is completed. They represent three different types of structures. CDOXY I is composed of chains, CDOXY II of discrete units, and CDOXY III of layers, in all cases held together by hydrogen bonds. There is O bridging between Cd atoms in CDOXY I and II and in CDOXY III too if the eighth O atom is counted. O bridging is met with in a number of Cd structures, e.g. Cd cyanoacetate (Post & Trotter, 1974a), Cd maleate dihydrate (Post & Trotter, 1974b), and Cd malonate monohydrate (Post & Trotter, 1974c). In the Cd diacetate dihydrate (Harrison & Trotter, 1972) infinite –O–Cd–O– spirals are formed. The Cd atoms



Fig. 3. The oxydiacetate ion. Figs. 1–3 were drawn by the program *ORTEP*.

are surrounded by seven O atoms forming pentagonal bipyramids in the three structures and in all cases the apices are formed by water O atoms. In CDOXY I the Cd—O distances vary from 2·278 (15) to 2·491 (14) and in CDOXY II from 2·236 (7) to 2·492 (8) Å, in good agreement with the values usually found. In these two structures coordination numbers and coordination polyhedra are fairly well-defined. In CDOXY III, however, with Cd—O distances between 2·269 (15) and 2·637 (15) or even 2·841 (13) Å, the situation is less clear-cut and the coordination number could also be taken as 8 or even as 6. Cd—O lengths in the literature vary between 1·98 (2) and 3·00 (2) Å and coordination numbers from 5 to 8 are known, as can be seen in the table compiled by Harrison & Trotter (1972). Some other cases with Cd coordinated by seven O atoms are known, e.g. the above-mentioned Cd diacetate dihydrate and Cd malonate monohydrate, the first with a distorted square-base–trigonal-cap geometry and the second with a distorted pentagonal-bipyramidal geometry. Also in $Cd(NO_3)_2.2H_2O$ (Milinski & Ribár, 1974) Cd is surrounded by seven O atoms forming a distorted pentagonal bipyramid.

The oxydiacetate ion occurs as a mono-, bi- and tridentate ligand in the Cd compounds. When it is bidentate either the ether O together with a carboxylate O or the two O atoms in one carboxylate group are used.

The conformation of the oxydiacetate ion in the solid state has been investigated in a number of compounds. The results are summarized by Herbertsson (1976), and from these it is seen that cations larger than $Na^+$ form tridentate chelates and that the oxydiacetate ions in these cases are planar. With smaller cations, e.g. $Li^+$, a bidentate chelate involving the ether O is formed. Cd with an ionic radius between $Li^+$ and $Na^+$ is found to form both tridentate and bidentate chelates and thus seems to be on the borderline. When a bidentate chelate involving the ether O is formed, the bite is smaller than the corresponding bite in a tridentate chelate and the oxydiacetate ion is more or less twisted about the ether O. This effect is most pronounced in CDOXY III.

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