and   N(21)—H(21)···O(13)—C(14)—O(14)···H(22) together with their centrosymmetrically related atoms. The rings have atoms in common and, as a result of this, 18-membered rings are also formed. The infinite chains are cross-linked by O—H—O bonds and by the interaction between O and Rb$^+$ in a three-dimensional structure. There are nine O atoms around the Rb$^+$ ion, eight of them situated at distances 2·985 (5) to 3·199 (6) Å and the ninth at the considerably longer distance 3·534 (6) Å, Table 3. The cations are held together in pairs through four O atoms, and these pairs are in their turn linked parallel to **b** by two O atoms (Fig. 2). One ligand forms an eight-membered chelate by coordination of two carboxylate oxygens, O(12) and O(14), to Rb$^+$. The cation takes part in six and seven-membered rings involved in the hydrogen-bond system.

The two independent iminodiacetic acid molecules have lost one proton and are connected through a bond of type O—H—O, with O—O = 2·445 (7) Å, as well as through the N—H—O bonds along **b**. The H atom in the O—H—O bond could not be located, but a neutron diffraction study is planned in order to decide if the hydrogen bond is symmetrical or not. As with monoclinic iminodiacetic acid the two ligands are zwitterions, which makes the hydrogen-bond system very complex. The negative charge is most probably spread over the carboxylate groups O(13)—C(14)—O(14) and

O(23)—C(24)—O(24). The dimensions of the other carboxyl groups indicate double bonds C(12)—O(12) and C(22)—O(22) and single bonds C(12)—O(11) and C(22)—O(21). Relevant distances and angles are listed in Table 4 and it can be seen that the main difference between the ligands involves O(12)···O(14), 4·150 (8) Å, and O(22)···O(24), 5·047 (8) Å, owing to the fact that ligand 1 forms a chelate with Rb$^+$. From the dihedral angles (Table 4) and the deviations from the least-squares planes (Table 5) through the ligand-halves it is obvious that ligand 2 is the more planar.

Fig. 3 shows the ligands with hydrogen bonds.

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The Structure of Orthorhombic Cadmium Oxydiacetate Trihydrate

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The structure of orthorhombic CdO(CH$_2$COO)$_2$.3H$_2$O has been determined from counter data. The space group is $P2_12_12_1$ with $a = 7·3934$ (7), $b = 8·8955$ (10), $c = 13·3536$ (15) Å, $Z = 4$. The structure ($R = 0·054$) consists of layers of composition CdO(CH$_2$COO)$_2$.2H$_2$O joined by hydrogen bonds *via* water molecules. Each Cd atom coordinates seven or possibly eight O atoms. The seven closest O atoms form a pentagonal bipyramid with coordination distances between 2·27 (1) and 2·64 (1) Å and the eighth O is situated at 2·84 (1) Å. The oxydiacetate ion is twisted and the CCOCC framework has the *trans–gauche* conformation. The non-hydrogen atoms are coplanar in each of the two oxydiacetate halves with an angle of 84° between the planes. The absolute configuration has been determined.

Introduction

This work forms part of an investigation of the co-ordination about Cd in compounds CdA.nH$_2$O, where A^{2-} represents the oxydi-, thiodi- or iminodiacetate ion. Several structures containing these anions in dif-

ferent environments have already been determined (Albertsson, 1972; Albertsson, Grenthe & Herbertsson, 1973*a,b*; Malmborg & Oskarsson, 1973; Oskarsson, 1974; Whitlow, 1975; Herbertsson, 1976), and the present investigation should give some new information about the geometry and chelating ability of the dif-

ferent ligands. In order to get more material for comparison and more accurate interatomic distances the structures of oxydiacetic acid (Herbertsson & Boman, 1973) and iminodiacetic acid (Boman, Herbertsson & Oskarsson, 1974) were determined. Thiodiacetic acid was investigated earlier (Paul, 1967).

Three different oxydiacetates, one thiodiacetate and two iminodiacetates of Cd have been prepared. The latter two seem, however, to be affected by disorder. Boman (1974) gave some preliminary data for the three Cd oxydiacetates, denoted CDOXY I, CDOXY II and CDOXY III. In this paper a detailed description of CDOXY III will be presented.

Crystal data

Diaquacadmium oxydiacetate monohydrate, $CdC_4H_{10}O_8$ (CDOXY III); F.W. 298·5 g mol^{-1}; orthorhombic, space group $P2_12_12_1$; $a = 7·3934$ (7), $b = 8·8955$ (10), $c = 13·3536$ (15) Å, $V = 878·2$ Å^3; $Z = 4$; μ(Cu $K\alpha$) = 208·9 cm^{-1}; $D_m = 2·21$, $D_x = 2·26$ g cm^{-3}. Numbers in parentheses are estimated standard deviations.

Experimental

The preparation of the colourless crystals, prismatic a, has been described (Boman, 1974). Elemental analyses and complexometric determination of Cd gave values in good agreement with those calculated from the formula. The density was obtained from the loss of weight in benzene.

From Weissenberg photographs it was concluded that the crystals are orthorhombic. The only space group consistent with the systematic absences, $h00$ with $h \neq 2n$, $0k0$ with $k \neq 2n$ and $00l$ with $l \neq 2n$, is $P2_12_12_1$. The preliminary cell dimensions obtained from Weissenberg photographs were refined by least squares from powder data from a Guinier–Hägg camera of radius 5·00 cm (Cu $K\alpha_1$ radiation, $\lambda = 1·54051$ Å). Al (cubic, $a = 4·04934$ Å, 22°C) was used as internal standard.

A crystal 0·35 × 0·12 × 0·05 mm was mounted along **a**. 600 independent reflexions, *i.e.* 60% of those possible, with sin$\theta/\lambda \leq 0·563$ (layers $0kl$–$6kl$) were measured with the ω-scan technique at 25°C on a Pailred diffractometer. The intensities of 42 reflexions with $I < 3\sigma_c(I)$ were given zero weight in the refinement. I is the net intensity obtained in a scan and $\sigma_c(I)$ is based on counting statistics. The monochromatic Cu $K\alpha$ radiation used was obtained by reflexion from the (002) planes of a graphite crystal. Four standard reflexions for each layer showed variations of less than 3% over each 24 h period.

The values of I and $\sigma_c(I)$ were corrected for absorp-

tion, polarization and the Lorentz effect. The transmission evaluated by numerical integration varied from 0·201 to 0·373.

Structure determination and refinement

The position of the Cd atom was determined from a Patterson synthesis. The remaining non-hydrogen atoms were located in subsequent difference syntheses. The H atoms could not be found.

Full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$ was performed with weights $w = 1/(\sigma_c^2 + a|F_o|^2)$, where a was chosen to make the average values as equal as possible in the different $|F_o|$ and sin θ intervals. In the last cycles of refinement the value of a was 0·004. 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, corresponding to a total of 118 parameters. The scattering factors for Cd were those given by Cromer & Waber (1965) and for C and O those of Hanson, Herman, Lea & Skillman (1964), in all cases for the neutral atoms. When correction for anomalous dispersion was made for Cd with $\Delta f' = -0·56$ and $\Delta f'' = 4·62$ (Cromer, 1965) one of the two possible enantiomorphous arrangements gave a lower R and was therefore chosen as the true absolute configuration. The final value of R was 0·054 and of R_w 0·072, with shifts less than 1% of the estimated standard deviations. A final difference map showed residual electron densities of about 1·9 e Å^{-3} in the vicinity of the Cd position but was otherwise featureless. A refinement including the methylene H atoms at calculated positions was not successful. No correction for extinction was made.

The atomic coordinates are listed in Table 1. The thermal parameters and the r.m.s. components along the principal axes of thermal displacement ellipsoids are given in Table 2.*

All computations were made on the Univac 1108 in Lund, Sweden (Oskarsson, 1973).

Description of the structure

The structure is shown in Fig. 1. Infinite layers of composition $CdO(CH_2COO)_2.2H_2O$ parallel to the ab plane are held together in the **c** direction by hydrogen bonds *via* the non-coordinated water O(8). Within the layers, the O atoms in the carboxylate group O(2)—

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32115 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates with standard deviations* (× 10⁴) *and isotropic temperature factors*

	x	y	z	B (Å²)
Cd	918 (1)	5654 (1)	4868 (1)	2·4
O(1)	2803 (15)	4304 (14)	6124 (8)	2·5
O(2)	3349 (17)	7015 (15)	5436 (11)	3·7
O(3)	6000 (17)	7215 (14)	6161 (8)	3·1
O(4)	4477 (21)	2055 (16)	5046 (10)	4·2
O(5)	3739 (20)	331 (16)	6132 (12)	3·8
O(6)	−617 (14)	6122 (14)	6347 (8)	2·7
O(7)	2929 (18)	4323 (18)	3845 (8)	3·6
O(8)	5796 (17)	5932 (17)	2961 (11)	4·5
C(1)	4524 (27)	4978 (18)	6438 (13)	2·0
C(2)	4593 (22)	6472 (21)	5944 (11)	2·0
C(3)	2705 (25)	2763 (17)	6484 (13)	2·3
C(4)	3674 (24)	1672 (25)	5801 (16)	3·5

C(2)–O(3) bind one Cd atom each, thus connecting the coordination polyhedra around the Cd atoms in the **a** direction. Parallel to **b**, Cd atoms in adjacent unit cells are linked together by an oxydiacetate ion.

Fig. 2 shows the coordination around Cd. The polyhedron is best described as a distorted pentagonal bipyramid, the seven Cd–O distances ranging from 2·269 (15) to 2·637 (15) Å. An eighth O atom, O(2'), is situated at a considerably longer distance, 2·841 (13) Å, but this O atom which belongs to the carboxylate group mentioned earlier is firmly attached to another Cd atom at a distance of 2·296 (13) Å. All other Cd–O distances are larger than 4 Å, and the shortest Cd–Cd distance is 4·957 (2) Å. Coordination distances and other relevant distances and angles in the pentagonal

Table 2. *Anisotropic thermal parameters with standard deviations* (× 10⁴ *for* Cd; × 10³ *for* O *and* C)

The form of the temperature factor is $\exp(-\beta_{11}h^2 - \cdots -2\beta_{12}hk - \cdots)$. The r.m.s. components R (× 10³ Å) of thermal displacement along the ellipsoid axes are also listed.

|	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Cd	112 (3)	74 (2)	36 (1)	12 (2)	−9 (1)	−3 (1)	195	160	171
O(1)	16 (2)	7 (2)	3 (1)	3 (2)	−2 (1)	−1 (1)	236	150	160
O(2)	21 (3)	7 (2)	8 (1)	−1 (2)	−4 (1)	1 (1)	293	167	204
O(3)	12 (2)	13 (2)	4 (1)	2 (2)	0 (1)	0 (1)	230	179	187
O(4)	25 (3)	14 (2)	6 (1)	5 (2)	6 (1)	2 (1)	317	180	218
O(5)	21 (3)	7 (2)	8 (1)	2 (2)	5 (2)	1 (1)	310	169	204
O(6)	11 (2)	11 (2)	4 (1)	1 (2)	3 (1)	0 (1)	221	140	209
O(7)	20 (3)	14 (2)	4 (1)	−5 (3)	1 (1)	−2 (1)	280	176	202
O(8)	22 (3)	13 (2)	8 (1)	3 (2)	−4 (1)	0 (1)	300	198	232
C(1)	23 (4)	4 (2)	5 (1)	−6 (3)	−5 (2)	2 (1)	298	85	164
C(2)	9 (4)	15 (3)	2 (1)	−4 (3)	−2 (1)	1 (1)	258	95	163
C(3)	15 (4)	3 (2)	6 (1)	3 (2)	1 (2)	0 (1)	242	98	204
C(4)	9 (4)	16 (4)	7 (1)	2 (3)	2 (2)	2 (2)	279	146	226
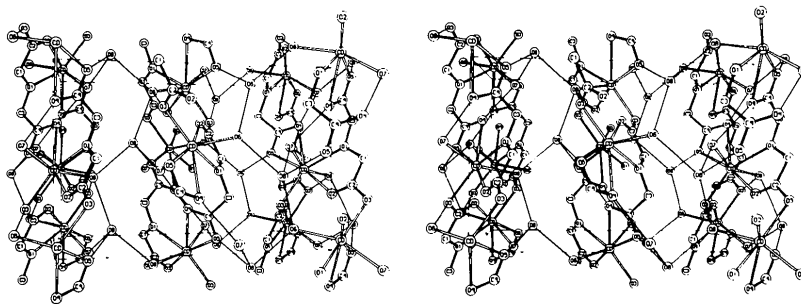
Fig. 1. A stereoscopic view of the structure of orthorhombic cadmium oxydiacetate trihydrate with the hydrogen bonds marked by thin lines. Figs. 1–3 were drawn by the program *ORTEP*.
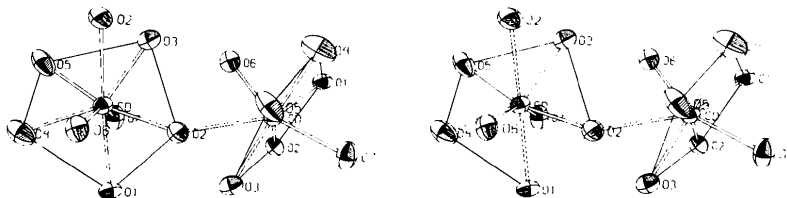

Fig. 2. The coordination around two neighbouring Cd atoms. The pentagons are marked by thin lines. In Figs. 2 and 3 thermal ellipsoids were used.

bipyramid are given in Table 3. The first five Cd—O distances are those to the O atoms forming the pentagon and the following two those of the O atoms forming the apices. The latter two, O(6) and O(7), belong to the coordinated water molecules. As seen from the superscripts in Table 3 three different oxydiacetic ions are involved in the coordination; two of them are bidentate with bites O(1)—O(2) 2·613(18) and O(4)—O(5) 2·180(21) Å. Deviations from the least-squares plane through the five equatorial O atoms are given in Table 4.

The oxydiacetate ion, Fig. 3, is twisted about the ether O and has the *trans–gauche* conformation. In most structures the oxydiacetate group has been found to be almost planar, the only known exceptions being monoclinic oxydiacetic acid (Davey & Whitlow,

1973; Herbertsson & Boman, 1973) and lithium hydrogen oxydiacetate (Herbertsson, 1976). The non-hydrogen atoms in each half of the oxydiacetate ion in CDOXY III are nearly coplanar and the angle be-
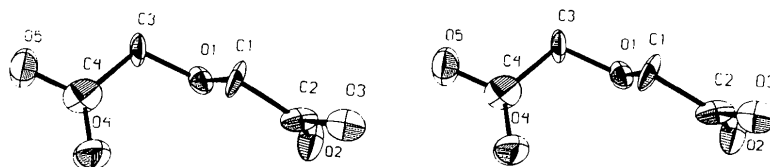
Table 5. *Interatomic distances (Å) and angles (°) for the oxydiacetate ion*

O(1)—C(1)	1·468(22)	C(1)—O(1)—C(3)	109·5 (1·2)
O(1)—C(3)	1·454(19)	O(1)—C(1)—C(2)	105·6 (1·4)
C(1)—C(2)	1·485 (24)	O(1)—C(3)—C(4)	112·4 (1·4)
C(3)—C(4)	1·512 (27)	C(1)—C(2)—O(2)	124·5 (1·6)
C(2)—O(2)	1·241 (21)	C(1)—C(2)—O(3)	113·2 (1·5)
C(2)—O(3)	1·266 (21)	O(2)—C(2)—O(3)	122·1 (1·7)
C(4)—O(4)	1·219 (25)	C(3)—C(4)—O(4)	123·4 (1·9)
C(4)—O(5)	1·273 (26)	C(3)—C(4)—O(5)	114·3 (1·7)
O(2)—O(3)	2·193 (18)	O(4)—C(4)—O(5)	122·1 (1·9)
O(4)—O(5)	2·180 (21)		
O(1)—O(2)	2·613 (18)		
O(1)—O(4)	2·757 (19)		
O(2)—O(4)	4·520 (20)		

Dihedral angles

O(1)—C(1)—C(2)—O(2)	4·4
O(1)—C(1)—C(2)—O(3)	178·6
O(1)—C(3)—C(4)—O(4)	1·5
O(1)—C(3)—C(4)—O(5)	174·7

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

The superscripts indicate transformations applied to the coordinates given in Table 1:

(i) $-1 + (\frac{1}{2} + x)$, $1 + (\frac{1}{2} - y)$, $1 - z$; (ii) $-1 + (\frac{1}{2} + x)$, $\frac{1}{2} - y$, $1 - z$.

Cd—O(1)	2·490 (11)	O(1)—Cd—O(2)	66·0 (4)
Cd—O(2)	2·296 (13)	O(2)—Cd—O(3ⁱ)	75·3 (5)
Cd—O(3ⁱ)	2·342 (12)	O(3ⁱ)—Cd—O(5ⁱⁱ)	89·2 (5)
Cd—O(5ⁱⁱ)	2·269 (15)	O(5ⁱⁱ)—Cd—O(4ⁱⁱ)	52·1 (5)
Cd—O(4ⁱⁱ)	2·637 (15)	O(4ⁱⁱ)—Cd—O(1)	75·9 (4)
Cd—O(6)	2·316 (11)	O(6)—Cd—O(7)	154·2 (4)
Cd—O(7)	2·341 (13)		
Cd—O(2ⁱ)	2·841 (13)		
O(1)—O(2)	2·613 (18)	O(4ⁱⁱ)—O(1)—O(2)	107·5 (5)
O(2)—O(3ⁱ)	2·834 (18)	O(1)—O(2)—O(3ⁱ)	113·1 (6)
O(3ⁱ)—O(5ⁱⁱ)	3·237 (19)	O(2)—O(3ⁱ)—O(5ⁱⁱ)	95·8 (5)
O(5ⁱⁱ)—O(4ⁱⁱ)	2·180 (21)	O(3ⁱ)—O(5ⁱⁱ)—O(4ⁱⁱ)	118·8 (7)
O(4ⁱⁱ)—O(1)	3·154 (19)	O(5ⁱⁱ)—O(4ⁱⁱ)—O(1)	104·8 (7)
O(6)—O(1)	3·017 (16)	O(7)—O(1)	3·045 (15)
O(6)—O(2)	3·272 (17)	O(7)—O(2)	3·216 (19)
O(6)—O(3ⁱ)	3·851 (16)	O(7)—O(3ⁱ)	3·394 (20)
O(6)—O(5ⁱⁱ)	3·585 (20)	O(7)—O(5ⁱⁱ)	3·113 (20)
O(6)—O(4ⁱⁱ)	3·384 (19)	O(7)—O(4ⁱⁱ)	3·195 (20)

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

Atoms defining the planes are those listed. The angle between the planes is 84°.

	Plane I		Plane II
O(1)	0·003	O(1)	−0·023
C(1)	−0·012	C(3)	0·019
C(2)	0·029	C(4)	0·039
O(2)	−0·012	O(4)	−0·004
O(3)	−0·007	O(5)	−0·030

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

O(1)	0·033	O(4ⁱⁱ)	−0·021
O(2)	−0·034	Cd*	−0·202
O(3ⁱ)	0·017	O(6)*	−2·402
O(5ⁱⁱ)	0·004	O(7)*	2·115

* Atoms not defining the plane.

Table 7. *Hydrogen-bond distances (Å)*

O(6)—H···O(3)	2·695 (16)
O(6)——H——O(8)	2·829 (19)
O(6)——H——O(8)	2·969 (19)
O(7)—H···O(4)	2·820 (20)
O(7)—H···O(8)	2·817 (19)
O(8)—H···O(5)	2·732 (20)
O(8)——H——O(6)	2·829 (19)
O(8)——H——O(6)	2·969 (19)
O(8)···H—O(7)	2·817 (19)

Fig. 3. The oxydiacetate ion.

tween the planes is 84 °, while the corresponding angle is 72° in the acid and 60° in the Li compound. Table 5 lists the dihedral angles as well as the interatomic distances and angles in the oxydiacetate ion, and the deviations from planarity in the two halves are shown in Table 6.

The O—O distances in the hydrogen-bond system are given in Table 7. Two of the three independent water molecules are coordinated by Cd, while the third is situated between the layers, holding them together to form the three-dimensional structure. All water H atoms except two, marked $--H--$ in the table, can be assigned to definite O atoms by geometrical considerations.

A comparison between the three Cd oxydiacetate structures is postponed to a later publication.

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The Structure of Cadmium Oxydiacetate–Water (2 : 7)

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The structure of $2CdO(CH_2COO)_2.7H_2O$ has been determined by Patterson and Fourier methods and refined to $R = 0.110$ for 1814 visual intensities. The space group is $P2_1/c$ with $a = 7.3215(11)$, $b = 7.3012(8)$, $c = 37.1411(38)$ Å, $\beta = 90.673(11)°$, $Z = 4$. The crystals are built up from broad, endless chains of composition $2CdO(CH_2COO)_2.5H_2O$ parallel to **b**. The chains are linked together by an extensive hydrogen-bond system. The two independent Cd atoms coordinate seven O atoms each. The coordination polyhedra are in both cases somewhat distorted pentagonal bipyramids, which are held together two by two with one vertex shared. The coordination distances range from 2.278(15) to 2.491(14) Å. The shortest Cd–Cd distance is 4.738(2) Å. The two independent oxydiacetate ions are both slightly twisted about their ether O atoms, but the non-hydrogen atoms in the oxydiacetate halves are coplanar with angles of 20 and 9° between the planes.

Introduction

Preliminary data were reported for three different phases of Cd oxydiacetate by Boman (1974). One of them, the orthorhombic trihydrate denoted CDOXY III, has been described in detail (Boman, 1977). In this paper one of the two monoclinic phases, CDOXY I, will be described.

Crystal data

Cadmium oxydiacetate–water (2:7) or *catena*-μ-oxydiacetato-pentaaquaoxydiacetatodicadmium dihydrate, $Cd_2C_8H_{22}O_{17}$ (CDOXY I); F.W. 615.1 g mol^{-1}; monoclinic, space group $P2_1/c$; $a = 7.3215(11)$, $b = 7.3012(8)$, $c = 37.1411(38)$ Å, $\beta = 90.673(11)°$; $V = 1985.3$ Å^3; $Z = 4$; μ(Cu $K\alpha$) = 185.6 cm^{-1}; $D_m =$