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Dihydroxyacetone (DHA) monomer complexes with $CaBr_2$ and $CdCl_2$

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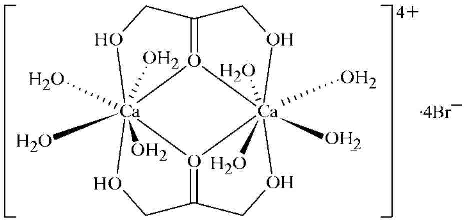
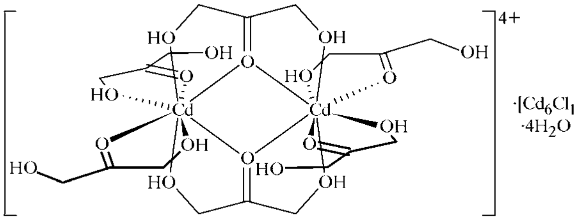
Two hydrated complexes of monomeric dihydroxyacetone (DHA; the simplest ketose), *viz.* the calcium bromide complex bis(μ-dihydroxyacetone)bis[tetraaquacalcium(II)] tetrabromide (isomorphous with the chloride compound reported previously), $[Ca_2(C_3H_6O_3)_2(H_2O)_8]Br_4$, (2*e*), and the cadmium chloride complex poly[[bis(μ-dihydroxyacetone)bis[bis(dihydroxyacetone)cadmium(II)]] [diaquatetradeca-μ-chlorido-dichloridohexacadmium(II)] tetrahydrate], $\{[Cd_2(C_3H_6O_3)_6][Cd_6Cl_{16}(H_2O)_2]\cdot 4H_2O\}_n$, (2*f*), are described. The Ca^{2+} or Cd^{2+} ions are bridged by the carbonyl O atoms from two DHA molecules to form centrosymmetric dimers, with Ca$\cdots$Ca distances of 4.334 (2) and 4.300 (2) Å in (2*e*), and a Cd$\cdots$Cd distance of 4.195 (1) Å in (2*f*). Almost identical in shape, the eight-coordinate polyhedra of the Ca^{2+} and Cd^{2+} ions are composed of $2n$ O atoms from n DHA molecules [$n = 2$ in (2*e*) and $n = 4$ in (2*f*)] and are completed by four water molecules in (2*e*). DHA molecules chelate the cations *via* both the hydroxyl and carbonyl groups and exist in an extended conformation, with both hydroxyl groups being synperiplanar to the carbonyl O atom. The crystal structures are stabilized by similar extensive O—H$\cdots$$X$ (X = Cl or Br) and O—H$\cdots$O hydrogen-bond networks involving all hydroxyl groups and the water molecules.

Comment

The solid-state study of dihydroxyacetone, DHA (1,3-dihydroxypropan-2-one), the simplest ketose, was undertaken as part of the structural characterization of the intermediates on a chemical pathway, based on the synthesis described by Ferroni *et al.* (1999) and then modified (Ślepokura & Lis, 2004*a*; Ślepokura, 2008), leading from dihydroxyacetone to its phosphate ester, dihydroxyacetone phosphate (DHAP), which is a biochemical intermediate of great biological and chemical (synthetic) importance (Gijsen *et al.*, 1996; Koeller & Wong, 2000; Machajewski & Wong, 2000; Fessner & Helaine, 2001). Previously, we have reported the crystal and molecular structures of the series of compounds occurring in the first six steps of the investigated pathway (Ślepokura & Lis, 2004*a*,*b*, 2006; Ślepokura, 2008).



(2*e*)



(2*f*)

DHA (ketotriose) and D-glyceraldehyde (aldotriose) are the basis of carbohydrate chemistry. Nevertheless, until 2004, the dimeric structure of D-glyceraldehyde, described in 1973 by Senma *et al.* (1973), was the only crystal structure of a triose given in the literature. In contrast with five- and six-carbon sugars, trioses and tetroses were poorly characterized in terms of their solid-state structure [see, for example, the Cambridge Structural Database (CSD), Version 5.29 of November 2007 (Allen, 2002)]. It is known that the commercial solid dihydroxyacetone, which is 100% in dimeric form, dissociates in water solution into a mixture of two monomeric forms, a free carbonyl (ketone, K) and a hydrate (*gem*-diol, H) in a ratio of 4:1 (Davis, 1973; Ślepokura & Lis, 2004*a*). Kobayashi *et al.* (1976) stated that in the melted state DHA also exists as a mixture of monomeric and dimeric molecules, the monomer being predominant. Nevertheless, the solid-state structure of dihydroxyacetone had not been reported until very recently, when we described its crystal and molecular structures in dimeric form, DHA-dimer [three polymorphous forms, (1*a*–*c*)], as well as in monomeric form [DHA, (2*c*)], along with two calcium chloride complexes of DHA, $[Ca_2Cl_2(DHA)_4(H_2O)_2]Cl_2$, (2*a*), and $[Ca_2(DHA)_2(H_2O)_8]Cl_4$, (2*b*) (Ślepokura & Lis, 2004*a*).

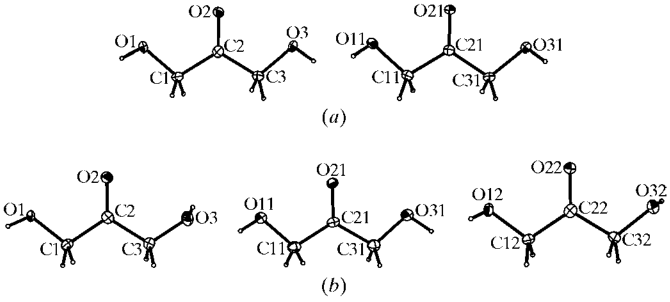


Figure 1
The molecular structures of the crystallographically independent DHA molecules in (*a*) (2*e*) and (*b*) (2*f*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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Analysis of the dihydroxyacetone calcium chloride complexes, (2*a*) and (2*b*), revealed very specific interactions between DHA molecules and Ca^{2+} cations. Although calcium complexation by α-hydroxycarboxylates is well known from the structural point of view, calcium complexation by α-hydroxyketones has only rarely been reported. The first crystallographic structural characterization of such a complex reported in the literature was the calcium complex of hydroxyacetophenone (phenacyl alcohol; Doxsee *et al.*, 1993). The α-hydroxyketone moiety occurs in a number of important pharmaceutical compounds (including corticosteroids and tetracycline antibiotics) and there have been reports suggesting the potential interaction of such pharmaceuticals with Ca^{2+} cations *in vivo* (Monder *et al.*, 1988; Lambs *et al.*, 1988).

The analysis of the structures of compounds (2*a–c*) reported by us previously (Ślepokura & Lis, 2004*a*) and those presented here, *viz*. (2*e*) and (2*f*), reveals a great similarity in the DHA molecules, regardless of whether they are coordinated to a metal centre or not. The overall molecular structure of monomeric dihydroxyacetone in the solid state is very rigid and hence almost identical in all its known compounds. The most important structural feature of all the DHA molecules is their planarity. The molecules exist in an extended (in-plane) conformation, with all of the non-H atoms lying in one plane, and with the hydroxyl H atoms being nearly coplanar in most cases. Both hydroxyl groups in compounds (2*a–f*) are in a synperiplanar (*sp*) orientation in relation to the carbonyl O atom. The molecular structures of the crystallographically independent DHA molecules, two in the calcium bromide complex, (2*e*), and three in the cadmium chloride complex, (2*f*), are shown in Fig. 1. The relevant torsion angles for all of them are listed in Tables 1 and 4. It is to be noted here that the synperiplanar orientation of the DHA hydroxyl and carbonyl groups was proposed by Yaylayan & Ismail (1995) on the basis of solution FT–IR spectroscopy. The planarity of the α-hydroxyketone moiety in the solid state has been observed in some steroids, *e.g.* cortisone and its derivatives (CSD; Allen, 2002), sugar derivatives, *e.g.* methyl 2-acetamido-2-deoxy-β-D-hexafuranosid-5-ulose (CSD refcode HANNOZ; Furneaux *et al.*, 1993), and hydroxyacetophenone complexed to the Ca^{2+} cation (Doxsee *et al.*, 1993). However, the steroid crystal structures show that when two α-hydroxyl groups are present relative to the ketone functionality, one of them adopts the antiperiplanar (*ap*) orientation.

The crystal structure of (2*e*) is isomorphous with that of (2*b*) and consists of $[Ca_2(DHA)_2(H_2O)_8]^{4+}$ cations with Br^- anions located between them. The crystal structure of (2*f*) is built up from $[Cd_2(DHA)_6]^{4+}$ cations, inorganic polymeric $\{[Cd_3Cl_8(H_2O)]^{2-}\}_n$ anions described below, and noncoordinated water of hydration. Two crystallographically independent Ca^{2+} cations in (2*e*) form two independent but chemically identical complex cations in a manner shown in Fig. 2. Two symmetry-related Ca^{2+} or Cd^{2+} ions are linked by two carbonyl O-atom bridges from two symmetry-related DHA molecules to form centrosymmetric dimers, with Ca···Ca distances of 4.334 (2) and 4.300 (2) Å in the two crystallographically independent

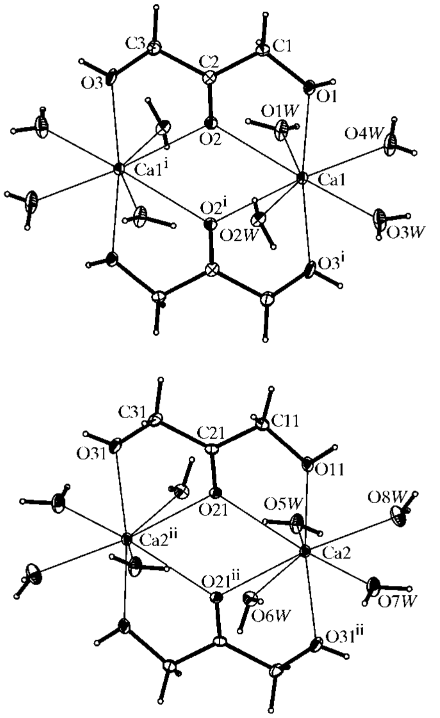


Figure 2
The molecular structures of the two crystallographically independent dimeric $[Ca_2(DHA)_2(H_2O)_8]^{4+}$ cations in (2*e*), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes are listed in Table 2.

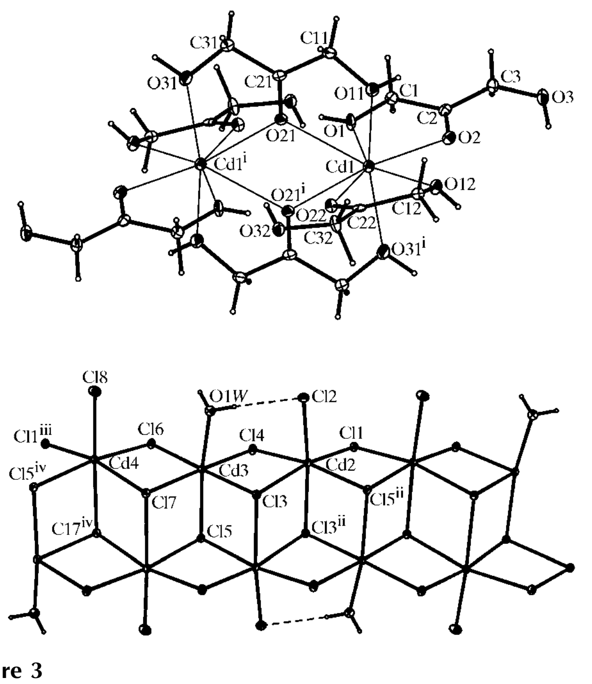


Figure 3
The molecular structures of the dimeric $[Cd_2(DHA)_6]^{4+}$ cation and polymeric $\{[Cd_3Cl_8(H_2O)]^{2-}\}_n$ anion in (2*f*), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The intraribbon O1*W*—H1*W*···Cl2 contacts in the anion are shown as dashed lines. Symmetry codes are listed in Table 5.

dimers in (2*e*) and a Cd$\cdots$Cd distance of 4.195 (1) Å in (2*f*). As found in (2*a*) and (2*b*) (Ślepokura & Lis, 2004*a*), the DHA molecules of the complex cations described here act as bridging as well as chelating ligands for two symmetry-related complex-forming metal centres (Figs. 2 and 3). Thus, the eight-coordinate polyhedra of each Ca^{2+} cation in (2*e*) and one of the Cd^{2+} cations (Cd1) in (2*f*) are composed of O atoms from the different number of DHA molecules coordinating to them [four O atoms from two DHA in (2*e*) and eight O atoms from four DHA in (2*f*)]. The coordination environments of the Ca^{2+} cations in (2*e*) are completed by four water molecules. The coordination polyhedra of the Ca^{2+} and Cd^{2+} metal centres may be described as distorted square antiprisms, with the longest of all the $M\cdots$O distances being the bridging distance $M\cdots$O2 (for geometry of the metal coordination spheres, see Tables 2 and 5). The same mode of coordination of the α-hydroxyketone moiety to Ca^{2+} or Cd^{2+} cations is observed in all the DHA complexes presented here and reported previously (Ślepokura & Lis, 2004*a*), as well as in hydroxyacetophenone complexed with CaCl$_2$ (Doxsee *et al.*, 1993). This coordination pattern is typical for the α-chelation mode, which is a characteristic mode for the interactions of α-hydroxyacids with Ca^{2+} ions (Einspahr & Bugg, 1981). In all the DHA complexes, there is a strong tendency for the M^{2+} ion to lie in the plane of the α-hydroxycarbonyl group, and therefore in the plane of the DHA molecules. The M^{2+} cations are restricted to a narrow region, with $M\cdots$O—C angles of about 110–130°, typical for the α-chelation mode, *viz.* 120.4 (2)–122.7 (2)° in (2*e*) and 117.8 (2)–122.4 (2)° in (2*f*).

The characteristic structural units of all the known DHA complexes are the complex cations, although these may be one of three different types. Identical cations with a 1:1 Ca^{2+}:DHA ratio (type I) are formed in the isomorphous crystal structures (2*b*) and (2*e*). Cations with a 1:2 Ca^{2+}:DHA ratio (type II) are present in the CaCl$_2$ complex, (2*a*). [It is to be noted here that the model obtained for the crystal structure of the CaBr$_2$ complex, (2*d*), reveals a similar complex cation.] The third type of dimeric cation is formed in the case of Cd centres, with a 1:3 Cd^{2+}:DHA ratio (type III). In all types of complex cation, the ligands (DHA and/or water molecules) are located on two almost perpendicular planes, intersecting each other along the line linking the two M^{2+} ions. The first of these is always built up from the two M^{2+} ions and two bridging DHA molecules to form the core of the dimeric complex cation. In general, the core plane is almost planar (deviations from the least-squares planes are less than 0.2 Å) in all the dimeric complex cations described. The second plane is composed of the same two M^{2+} ions and the other, chelating, DHA molecules and/or water molecules [Cl$^-$ in (2*a*)]. This plane is quite well defined in the complex cation of type II. The same plane in complex cations of types I (eight water molecules) and III (four DHA molecules) is much less well defined, with O6*W* water molecules in (2*b*) and (2*e*) being displaced from the plane by 0.4–0.5 Å, and with some of the atoms in (2*f*) deviating by 0.2–0.3 Å. The intersection angles between the two planes are 87.9 (1) and 88.1 (1)° in the two crystallographically independent complex cations formed by Ca1 and Ca2 in (2*e*), and 83.3 (1)° in (2*f*).

The great similarity in the building of Ca^{2+} and Cd^{2+} complex cations in (2*a*), (2*b*), (2*e*) and (2*f*) may have some biological justification. It is known that Cd^{2+} ions, despite their different chemical nature, may mimic Ca^{2+} ions in terms of their interactions with the sugar moiety, *e.g.* in nucleotide anions (Goodgame *et al.*, 1975). Cadmium toxicity is also well known, causing kidney and liver dysfunction and brittle bones.

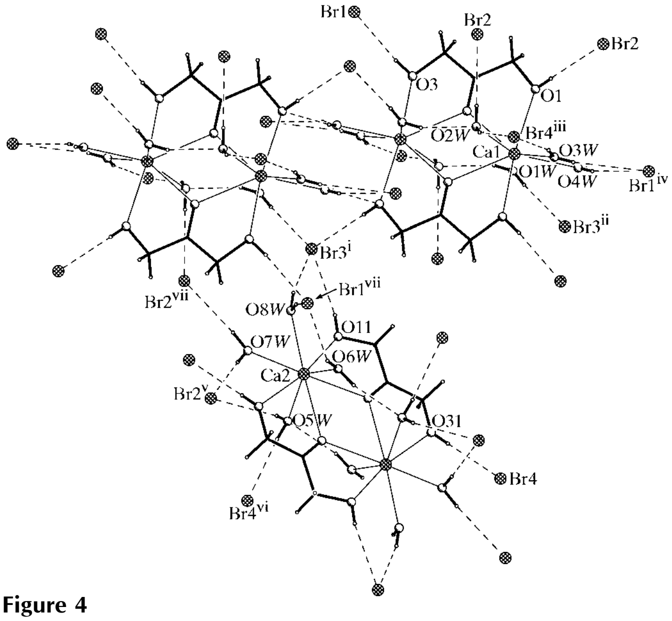


Figure 4
The arrangement of the complex dimers in (2*e*), with the Br-bridged interdimeric O—H$\cdots$Br$\cdots$H—O linkages of the dimers shown as dashed lines. Symmetry codes are given in Table 3.

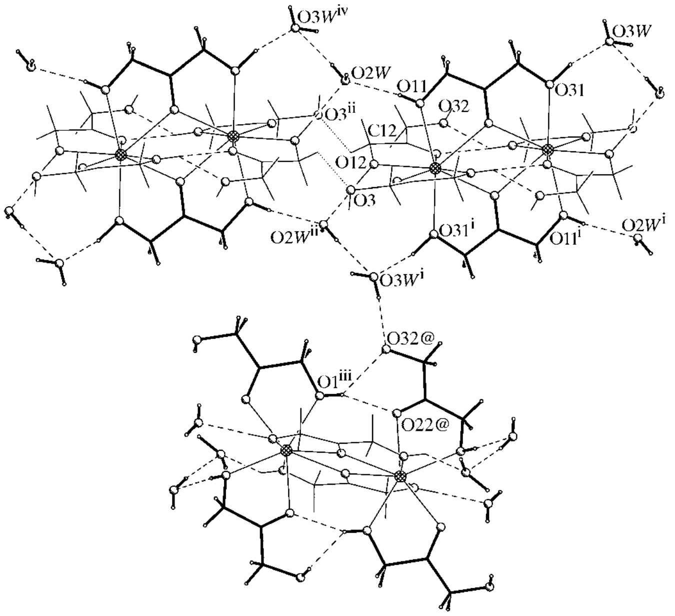


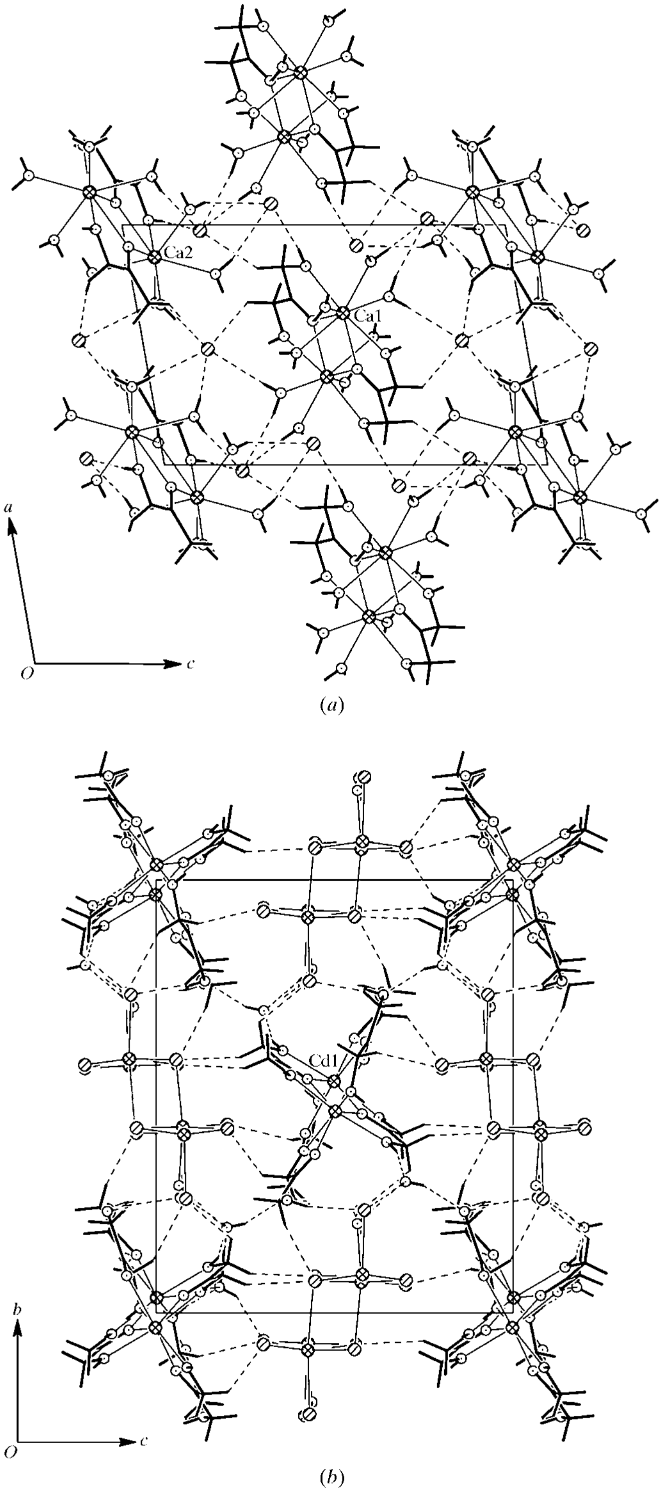
Figure 5
The arrangement of the complex dimers in (2*f*), with the water-bridged interdimeric interactions shown as dashed lines and the direct C12—H12*B*$\cdots$O3^{ii} interactions shown as dotted lines. Symmetry codes are given in Table 6; additionally, an 'at' symbol (@) denotes atoms generated by the symmetry operator $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$.

Cadmium competes with calcium both in calcium channels and in intracellular calcium-binding proteins (Richardt *et al.*, 1986; Hinkle *et al.*, 1987).

As observed in the previously presented DHA complexes, as well as in free DHA crystals (Ślepokura & Lis, 2004*a*), all hydroxyl groups of the DHA molecules of the calcium bromide, (2*e*), and cadmium chloride, (2*f*), complexes are involved in medium–strong and weak hydrogen bonds of diverse type, mainly as donors, but also as acceptors (Figs. 4–6, and Tables 3 and 6). Adjacent complex dimers are linked to each other by two kinds of interactions, direct (between the dimers) and indirect (through the halide or/and water bridges). Although the overall crystal packing mode of (2*f*) seems to be different from that observed in the calcium halide complexes, due to the presence of polymeric inorganic anions, in fact they reveal great similarity, mainly in the geometry of the interdimeric interactions described in detail below.

Two of the calcium halide complexes, (2*b*) and (2*e*), are isomorphous, and an analogous, almost identical, pattern of O—H$\cdots$O, O—H$\cdots$*X* and C—H$\cdots$*X* hydrogen bonds is observed in their crystal structures. In general, both hydroxyl groups of the DHA molecules in the $\mathrm{Ca}X_2$ complexes, (2*a*), (2*b*) and (2*e*), form one O—H$\cdots$*X* contact, except for one of the OH groups in (2*a*), which is involved in interdimeric O—H$\cdots$O interactions instead. The same halide anion is simultaneously linked to the other DHA or water molecule from an adjacent complex dimer. The DHA$\cdots$*X* interactions are almost linear in most cases, which means that the halide anions lie almost in planes, in which the DHA molecules are located. Thus, the O—H$\cdots$*X* network links adjacent cationic dimers *via* Cl^- or Br^- bridges. The water molecules are involved in similar O—H$\cdots$*X* interactions linking adjacent complex cations. In (2*e*), all the Br^- anions act as bridges between every three adjacent complex cations, forming different types of interdimeric O—H$\cdots$Br$\cdots$H—O interactions: water$\cdots$Br$\cdots$water (for Br1, Br2 and Br4), DHA$\cdots$Br$\cdots$water (Br1, Br3 and Br4) or DHA$\cdots$Br$\cdots$DHA (Br3). Thus, a three-dimensional network of furcated five- (for Br2, Br3 and Br4) or six-centred (for Br1) O—H$\cdots$Br hydrogen bonds is formed. Additionally, each dimer is stabilized by intradimeric water–water O—H$\cdots$O interactions (Fig. 4 and Table 3).

The chief characteristic of the packing mode in the cadmium chloride complex, (2*f*), is a three-dimensional network of O—H$\cdots$O hydrogen bonds (Fig. 5 and Table 6). The counter-ions for the dimeric cations in (2*f*) are the inorganic polymeric anionic $\{[\mathrm{Cd_3Cl_8(H_2O)}]^{2-}\}_n$ ribbons along the *a* axis, the structure of which consists of edge-sharing $\mathrm{CdCl_6}$ (for Cd2 and Cd4) and $\mathrm{CdCl_5(H_2O)}$ (for Cd3) octahedra. Each ribbon is built up from two antiparallel chains by sharing the edges of the respective octahedra from the two chains in a manner shown in Fig. 3. The Cd—Cl distances are in the ranges 2.535 (1)–2.759 (1) and 2.541 (1)–2.792 (1) Å for the $\mathrm{CdCl_6}$ units (Cd2 and Cd4, respectively), and 2.552 (1)–2.678 (1) Å for the hydrated unit (Cd3) (Table 5). Since all the Cl^- ions are coordinated to the Cd^{2+} cations forming the anionic ribbon, the role of the O—H$\cdots$Cl interactions also present in the crystal structure is to link the organometallic and inorganic parts with each other. Thus, each complex cation is linked to the inorganic $\{[\mathrm{Cd_3Cl_8(H_2O)}]^{2-}\}_n$ ribbon by means of three O—H$\cdots$Cl interactions formed by two DHA molecules and one water molecule. Nevertheless, one can see several common features in all the calcium halide and



(*a*)

(*b*)

Figure 6
The crystal packing modes in the structures of (*a*) (2*e*) and (*b*) (2*f*).

cadmium chloride DHA complexes. Water molecules O2*W* and O3*W* in (2*f*) adopt the role played by Cl^- and Br^- ions in the crystal structures of the CaX_2 complexes. Adjacent dimeric cations are linked to each other by O—H···O2*W*···H—O (DHA···water···DHA) water bridges and interdimeric C—H···O (DHA···DHA) contacts to form columns along the *a* axis (Fig. 6). Adjacent organometallic columns are joined to each other by DHA···O3*W*···DHA and DHA···O2*W*···O3*W*···DHA interactions. Thus, water molecule O3*W* acts as an interdimeric as well as an inter-column bridge. Furthermore, it is involved in O1*W*—H2*W*···O3*W*^{i} interactions joining the organometallic and inorganic parts of the compound, and hence is crucial for stabilizing the crystal structure of (2*f*). The DHA molecules within one complex cation of (2*f*) (located on the same plane) interact with each other by means of bifurcated three-centred intradimeric O—H···O hydrogen bonds (O1—H1···O22^{i} and O1—H1···O32^{i}, shown in Fig. 5 as O1^{iii}—H1^{iii}···O22$^{@}$ and O1^{iii}—H1^{iii}···O32$^{@}$).

Experimental

Large colourless plates of (2*e*) were obtained by slow evaporation of an aqueous solution containing a 1:0.5 molar ratio mixture of commercial $CaBr_2 \cdot 2H_2O$ (131 mg) and DHA-dimer (50 mg) at 277 K. The specimen used for X-ray diffraction measurements was obtained by cutting an appropriate fragment from a large crystal of (2*e*). When starting with substrate ratios of 1:1 and 1:2, another complex of DHA with $CaBr_2$ was formed, denoted (2*d*). Differential scanning calorimetry experiments on crystals of (2*d*) revealed a phase transition at about 200 K. It proceeds differently during cooling and heating of the crystals and reveals a series of several broad transitions. Nevertheless, the diffraction patterns obtained from the same or/and different crystals of (2*d*) at different temperatures were always similar, regardless of the speed of change of the temperature. Analysis of the Ewald sphere revealed the systematic occurrence of weak reflections, trebling the cell volume. Most probably, these weak reflections result from modulation rather than from superstructure. Omitting all the weak reflections gave only an approximate model of the compound, with the formula $[Ca_2(DHA)_4(H_2O)_4]Br_4 \cdot 0.6H_2O$, and this is not presented in this paper.

Slow evaporation at 277 K of aqueous solutions containing different mixtures of $CdCl_2 \cdot 2.5H_2O$ and commercial DHA-dimer (molar ratios 1:0.5, 1:1 and 1:2) always gave large colourless parallelepipeds (with a tendency to twinning) of a cadmium complex of DHA of the same composition, *viz*. $[Cd_2(DHA)_6][Cd_6Cl_{16}(H_2O)_2] \cdot 4H_2O$, (2*f*). A small single crystal from the 1:1 sample (63.4 mg $CdCl_2 \cdot 2.5H_2O$ and 50 mg DHA-dimer) was chosen for X-ray diffraction data collection.

Table 1
Selected geometric parameters (Å, °) for (2*e*).

O1—C1	1.425 (3)	O11—C11	1.419 (3)
O2—C2	1.225 (3)	O21—C21	1.221 (3)
O3—C3	1.419 (3)	O31—C31	1.416 (3)
O1—C1—C2—O2	−4.2 (3)	O11—C11—C21—O21	−7.7 (3)
O1—C1—C2—C3	175.4 (2)	O11—C11—C21—C31	170.1 (2)
O2—C2—C3—O3	−8.1 (3)	O21—C21—C31—O31	−9.6 (3)
C1—C2—C3—O3	172.3 (2)	C11—C21—C31—O31	172.6 (2)

Complex (2e)

Crystal data

$[Ca_2(C_3H_6O_3)_2(H_2O)_8]Br_4$
$M_r = 724.08$
Triclinic, $P\overline{1}$
$a = 9.225$ (2) Å
$b = 9.143$ (2) Å
$c = 14.504$ (3) Å
$\alpha = 90.73$ (3)°
$\beta = 100.01$ (3)°
$\gamma = 92.84$ (3)°
$V = 1202.9$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 7.17$ mm^{-1}
$T = 100$ (2) K
0.41 × 0.36 × 0.17 mm

Data collection

Kuma KM-4 κ-geometry diffractometer with Sapphire CCD camera
Absorption correction: analytical (*CrysAlis RED* in *KM-4 CCD Software*; Oxford Diffraction, 2004)
$T_{min} = 0.100$, $T_{max} = 0.283$
18605 measured reflections
6788 independent reflections
5914 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.057$
$S = 1.04$
6788 reflections
326 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 2
The coordination environment of the Ca^{2+} ions in (2*e*) (Å).

Ca1—O1	2.458 (2)	Ca2—O11	2.420 (2)
Ca1—O2	2.524 (2)	Ca2—O21	2.512 (2)
Ca1—O2^{i}	2.574 (2)	Ca2—O21^{ii}	2.550 (2)
Ca1—O3^{i}	2.387 (2)	Ca2—O31^{ii}	2.402 (2)
Ca1—O1*W*	2.351 (2)	Ca2—O5*W*	2.450 (2)
Ca1—O2*W*	2.439 (2)	Ca2—O6*W*	2.380 (2)
Ca1—O3*W*	2.405 (2)	Ca2—O7*W*	2.380 (2)
Ca1—O4*W*	2.388 (2)	Ca2—O8*W*	2.431 (2)
Ca1···Ca1^{i}	4.334 (2)	Ca2···Ca2^{ii}	4.300 (2)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y-z$.

Table 3
Hydrogen-bond geometry (Å, °) for (2*e*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Br3	0.77 (4)	2.39 (4)	3.150 (2)	169 (4)
O3—H3···Br1	0.84 (4)	2.33 (4)	3.159 (2)	172 (4)
O11—H11···Br3^{i}	0.77 (4)	2.48 (4)	3.222 (2)	162 (3)
O31—H31···Br4	0.78 (4)	2.43 (4)	3.206 (2)	173 (4)
O1*W*—H1*W*···Br3^{ii}	0.78 (5)	2.53 (5)	3.312 (2)	175 (4)
O1*W*—H2*W*···O2*W*^{i}	0.80 (4)	2.06 (4)	2.828 (3)	161 (4)
O2*W*—H4*W*···Br2	0.73 (4)	2.52 (4)	3.244 (2)	177 (4)
O2*W*—H3*W*···Br4^{iii}	0.82 (4)	2.57 (4)	3.340 (2)	157 (3)
O3*W*—H6*W*···Br1^{iv}	0.69 (4)	2.73 (4)	3.412 (2)	169 (4)
O3*W*—H5*W*···Br4^{iii}	0.84 (5)	2.47 (5)	3.288 (2)	163 (4)
O4*W*—H8*W*···Br1^{iv}	0.64 (5)	2.64 (5)	3.276 (3)	169 (5)
O4*W*—H7*W*···O1^{ii}	0.77 (5)	2.28 (5)	2.979 (3)	152 (4)
O5*W*—H10*W*···Br2^{v}	0.74 (4)	2.73 (4)	3.396 (2)	151 (4)
O5*W*—H9*W*···Br4^{vi}	0.82 (5)	2.49 (5)	3.298 (2)	170 (4)
O6*W*—H11*W*···Br1^{vii}	0.77 (4)	2.64 (4)	3.328 (2)	150 (4)
O6*W*—H12*W*···O5*W*^{viii}	0.83 (4)	2.10 (4)	2.840 (3)	149 (3)
O7*W*—H13*W*···Br2^{v}	0.78 (4)	2.54 (4)	3.321 (2)	175 (3)
O7*W*—H14*W*···Br2^{vii}	0.85 (5)	2.50 (5)	3.322 (2)	164 (4)
O8*W*—H15*W*···Br1^{vii}	0.82 (5)	2.59 (5)	3.387 (2)	165 (4)
O8*W*—H16*W*···Br3^{i}	0.78 (4)	2.66 (4)	3.401 (2)	160 (4)
C1—H1*B*···Br2	0.99	2.87	3.526 (3)	125
C3—H3*A*···Br4^{ix}	0.99	3.00	3.602 (3)	121
C11—H11*A*···Br2^{i}	0.99	2.95	3.794 (3)	144
C11—H11*B*···Br3^{v}	0.99	3.05	3.710 (3)	125
C31—H31*A*···Br2^{x}	0.99	3.13	3.785 (3)	125

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $x, y, z+1$; (iv) $x+1, y+1, z$; (v) $x, y-1, z-1$; (vi) $x, y-1, z$; (vii) $-x+1, -y, -z+1$; (viii) $-x+2, -y, -z$; (ix) $x-1, y, z+1$; (x) $x, y, z-1$.

Complex (2*f*)

Crystal data

$[Cd_2(C_3H_6O_3)_6][Cd_6Cl_{16}(H_2O)_2]\cdot 4H_2O$
M_r = 2114.96
Monoclinic, $P2_1/n$
a = 11.170 (3) Å
b = 17.119 (3) Å
c = 14.225 (3) Å
β = 95.42 (3)°
V = 2707.9 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.94 mm^{-1}
T = 100 (2) K
0.19 × 0.08 × 0.04 mm

Data collection

Kuma KM-4 κ-geometry diffractometer with Sapphire CCD camera
Absorption correction: analytical (*CrysAlis RED* in *KM-4 CCD Software*; Oxford Diffraction, 2004)
$T_{\min}$ = 0.550, $T_{\max}$ = 0.850
38913 measured reflections
7856 independent reflections
5800 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.036
S = 1.00
7856 reflections
322 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 1.02 e Å^{-3}
$\Delta\rho_{\min}$ = −0.60 e Å^{-3}

Table 4
Selected geometric parameters (Å, °) for (2*f*).

O1—C1	1.416 (3)	O31—C31	1.417 (3)
O2—C2	1.221 (3)	O12—C12	1.427 (3)
O3—C3	1.405 (3)	O22—C22	1.218 (3)
O11—C11	1.424 (3)	O32—C32	1.421 (3)
O21—C21	1.229 (3)		
O1—C1—C2—O2	2.6 (4)	O21—C21—C31—O31	6.4 (4)
O1—C1—C2—C3	−178.3 (2)	C11—C21—C31—O31	−172.9 (2)
O2—C2—C3—O3	0.3 (4)	O12—C12—C22—O22	−10.0 (4)
C1—C2—C3—O3	−178.7 (2)	O12—C12—C22—C32	172.5 (2)
O11—C11—C21—O21	−0.8 (4)	O22—C22—C32—O32	−5.6 (4)
O11—C11—C21—C31	178.5 (2)	C12—C22—C32—O32	171.9 (2)

Table 5
The coordination environment of the Cd^{2+} ions in (2*f*) (Å).

Cd1—O1	2.296 (2)	Cd3—O1*W*	2.341 (2)
Cd1—O2	2.383 (2)	Cd3—Cl3	2.6370 (11)
Cd1—O11	2.375 (2)	Cd3—Cl4	2.5613 (10)
Cd1—O21	2.502 (2)	Cd3—Cl5	2.6780 (8)
Cd1—O12	2.335 (2)	Cd3—Cl6	2.5516 (11)
Cd1—O22	2.360 (2)	Cd3—Cl7	2.6158 (11)
Cd1—O21$^{\rm i}$	2.432 (2)	Cd4—Cl6	2.5746 (10)
Cd1—O31$^{\rm i}$	2.370 (2)	Cd4—Cl7	2.6551 (12)
Cd1···Cd1$^{\rm i}$	4.1954 (11)	Cd4—Cl8	2.5414 (9)
Cd2—Cl1	2.5713 (10)	Cd4—Cl1$^{\rm iii}$	2.5726 (11)
Cd2—Cl2	2.5350 (9)	Cd4—Cl5$^{\rm iv}$	2.6572 (11)
Cd2—Cl3	2.6740 (11)	Cd4—Cl7$^{\rm iv}$	2.7925 (9)
Cd2—Cl4	2.5839 (11)	Cd2···Cd3	3.7147 (10)
Cd2—Cl3$^{\rm ii}$	2.7591 (9)	Cd3···Cd4	3.7252 (10)
Cd2—Cl5$^{\rm ii}$	2.6523 (12)	Cd4···Cd2$^{\rm iii}$	3.7544 (10)

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

Table 6
Hydrogen-bond geometry (Å, °) for (2*f*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O22$^{\rm i}$	0.84	2.07	2.822 (3)	150
O1—H1···O32$^{\rm i}$	0.84	2.45	3.073 (3)	131
O3—H3···Cl8	0.84	2.52	3.312 (2)	158
O11—H11···O2*W*	0.84	1.98	2.810 (3)	172
O31—H31···O3*W*	0.84	1.94	2.740 (3)	160
O12—H12···O2*W*$^{\rm ii}$	0.84	1.95	2.784 (3)	173
O32—H32···Cl2$^{\rm i}$	0.84	2.27	3.096 (2)	169
O1*W*—H1*W*···Cl2	0.80 (3)	2.41 (3)	3.203 (2)	176 (3)
O1*W*—H2*W*···O3*W*$^{\rm i}$	0.76 (4)	2.19 (4)	2.944 (3)	173 (4)
O2*W*—H3*W*···Cl4$^{\rm iii}$	0.74 (4)	2.74 (4)	3.302 (3)	134 (3)
O2*W*—H4*W*···O3*W*$^{\rm iv}$	0.77 (3)	2.20 (4)	2.955 (3)	170 (4)
O3*W*—H5*W*···Cl8$^{\rm i}$	0.98 (4)	2.09 (4)	3.067 (3)	174 (3)
O3*W*—H6*W*···O32$^{\rm v}$	0.76 (4)	1.96 (4)	2.690 (3)	159 (4)
C1—H1*A*···Cl1$^{\rm iii}$	0.99	3.11	3.630 (3)	114
C1—H1*A*···Cl6$^{\rm vi}$	0.99	2.88	3.570 (3)	127
C1—H1*A*···Cl8$^{\rm vi}$	0.99	3.17	4.099 (3)	157
C3—H3*A*···Cl7	0.99	2.79	3.545 (3)	134
C3—H3*B*···Cl1$^{\rm iii}$	0.99	3.02	3.574 (3)	117
C11—H11*B*···Cl2$^{\rm i}$	0.99	3.01	3.638 (3)	123
C11—H11*A*···Cl1$^{\rm iii}$	0.99	2.97	3.628 (3)	125
C11—H11*A*···Cl7$^{\rm vii}$	0.99	2.77	3.679 (3)	153
C31—H31*B*···Cl5$^{\rm vi}$	0.99	2.84	3.740 (3)	151
C31—H31*B*···Cl6$^{\rm vi}$	0.99	2.94	3.582 (3)	123
C31—H31*A*···Cl2$^{\rm i}$	0.99	2.83	3.459 (3)	122
C12—H12*A*···Cl8$^{\rm ii}$	0.99	2.78	3.643 (3)	146
C12—H12*B*···Cl4$^{\rm viii}$	0.99	2.81	3.379 (3)	117
C12—H12*B*···O3$^{\rm ii}$	0.99	2.62	3.204 (3)	118
C32—H32*B*···Cl5$^{\rm ix}$	0.99	3.03	3.693 (3)	126
C32—H32*B*···Cl8$^{\rm ii}$	0.99	2.79	3.689 (3)	151
C32—H32*A*···Cl4$^{\rm viii}$	0.99	3.05	3.667 (3)	121

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (viii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ix) $x, y+1, z$.

Since the calcium bromide complex (2*e*) is isomorphous with the calcium chloride complex (2*b*), the cell setting of (2*e*) was related to that of (2*b*), which resulted in nonstandard axial order. The refinement of the structure of (2*e*) was started using the heavy-atom coordinates from (2*b*). Two of the Br$^-$ ions in (2*e*) are slightly disordered over two positions, Br1/Br10 and Br2/Br20, with the occupancy factors being 0.975 (6) and 0.025 (6) for Br1 and Br10, respectively, and 0.982 (3) and 0.018 (3) for Br2 and Br20, respectively. Due to the low occupancy of Br10 and Br20, only the Br1 and Br2 positions are discussed. All of the non-H atoms were refined anisotropically, except for the low-occupied positions of the disordered atoms in (2*e*), *i.e.* Br10 and Br20.

All H atoms in (2*e*) and (2*f*) were found in difference Fourier maps. In the final refinement cycles, all O-bonded H atoms in (2*e*) were refined isotropically, while the remaining H atoms in (2*e*) and (2*f*) were positioned geometrically and treated as riding atoms, with C—H = 0.99 Å and O—H = 0.84 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(O). Water H atoms in (2*f*) were refined with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

For both complexes, data collection: *CrysAlis CCD* in *KM-4 CCD Software* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* in *KM-4 CCD Software*; data reduction: *CrysAlis RED* in *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3189). Services for accessing these data are described at the back of the journal.

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