metal-organic compounds

catena-Poly[bis[1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane] [cadmium(II)-tri-*μ*-chlorido-[chlorido-cadmium(II)]-di-*μ*-chlorido-[chlorido-cadmium(II)]-tri-*μ*-chlorido] tetra-hydrate]

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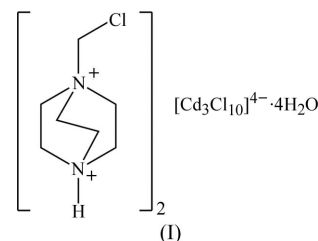
The title compound, $\{(C_7H_{15}N_2Cl)_2[Cd_3Cl_{10}]\cdot4H_2O\}_n$, consists of 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane dications, one-dimensional inorganic chains of $\{[Cd_3Cl_{10}]^{4-}\}_\infty$ anions and uncoordinated water molecules. Each of the two independent Cd^{II} ions, one with site symmetry $2/m$ and the other with site symmetry m, is octahedrally coordinated by chloride ions (two with site symmetry m and one with site symmetry 2), giving rise to novel polymeric zigzag chains of corner-sharing Cd-centred octahedra parallel to the c axis. The organic cations, bisected by mirror planes that contain the two N atoms, three methylene C atoms and the Cl atom, are ordered. Hydrogen bonds (O—H···Cl and O—H···O) between the water molecules (both with O atoms in a mirror plane) and the chloride anions of neighbouring chlorido-cadmate chains form a three-dimensional supramolecular network.

Comment

As part of the general interest in molecular-based materials with functional properties, attention has been devoted to one-, two- and three-dimensional chloridocadmate(II) compounds. One-dimensional chloridocadmate(II) inorganic chains show a great variety of architectures, such as the linear chains in $\{[Cd_2Cl_6]^{2-}\}_\infty$ (Schroder *et al.*, 1983; Corradi *et al.*, 1997; Costin-Hogan *et al.*, 2008), zigzag chains (Charles *et al.*, 1984; Corradi *et al.*, 1997) and ribbon-like chains (Rolies & De Ranter, 1978; Bats *et al.*, 1979; Corradi *et al.*, 1993; Thorn *et al.*, 2006). Against this background, we present here the title compound, (I), with a novel architecture of $\{[Cd_3Cl_{10}]^{4-}\}_\infty$ anionic chains. As the basic building unit, the linear $[Cd_3Cl_{10}]^{4-}$ trimer is interconnected by two bridging (corner-shared) chloride ions to form one-dimensional zigzag chains.

This unique chain structure is obviously modulated by the shape of the organic cations in (I).


$$[Cd_3Cl_{10}]^{4-}\cdot4H_2O$$

(I)

Compound (I) consists of 1-chloromethyl-1,4-diazonia-bicyclo[2.2.2]octane dications, one-dimensional inorganic anionic chains of composition $\{[Cd_3Cl_{10}]^{4-}\}_\infty$ and uncoordinated water molecules (Fig. 1). Two non-equivalent Cd^{II} ions are present in the chains with moderately distorted octahedral arrangements (Table 1). The Cd1 ion (Wyckoff site 2*d*, site symmetry $2/m$) is coordinated by six bridging chloride anions [Cl2, Cl2^{iii}, Cl3, Cl3^{iii}, Cl3^i and Cl3^{iv}; symmetry codes: (i) $-x+1, -y, -z+3$; (iii) $-x+1, y, -z+3$; (iv) $x, -y, z$], while the Cd2 ion (Wyckoff site 4*i*, site symmetry *m*) is surrounded by one terminal (Cl4) and five bridging (Cl2^{iii}, Cl3, Cl3^{iv}, Cl5 and Cl5^{iv}) chloride anions. The Cd1 and Cd2 ions are linked together by three chloride anions (Cl2^{iii}, Cl3 and Cl3^{iv}). The Cd2···Cd1···Cd2^{iii} and Cd1···Cd2···Cd1^{iv} angles within the chains are 180 and 135.92 (1)°, respectively, giving rise to zigzag chains of corner-sharing Cd-centred octahedra (Fig. 2).

The zigzag anionic chain in (I) is a new coordination architecture when compared with a similar compound, $(C_6H_5NH_3)_4[Cd_3Cl_{10}]$, which contains the same trimeric $[Cd_3Cl_{10}]^{4-}$ unit (Costin-Hogan *et al.*, 2008). In that compound, the linear trimers are assembled differently from those in (I), *i.e.* interconnected by bridging (corner-shared) chloride ions, with each trimer linking four other trimers to form a two-dimensional network. Other trimeric chlorido-cadmate anions have been described, such as $[Cd_3Cl_9]^{3-}$ in $(C_6H_5NH)_3[Cd_3Cl_9]$, in which the trimers are interconnected by three bridging (corner-shared) chloride ions to give rise to one-dimensional linear chains (Jian *et al.*, 2006).
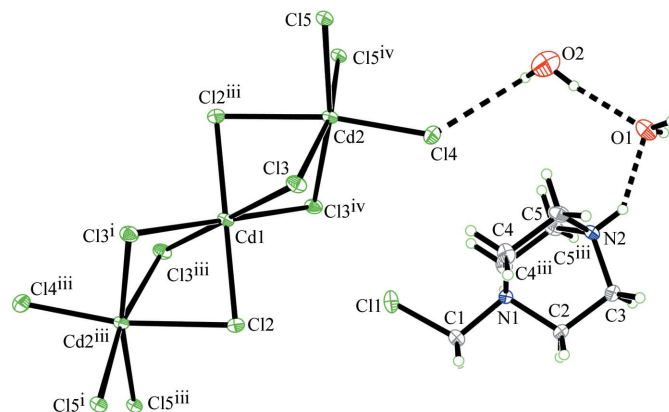
Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate the intramolecular hydrogen bonds. [Symmetry codes: (i) $-x+1, -y, -z+3$; (iii) $-x+1, y, -z+3$; (iv) $x, -y, z$.]
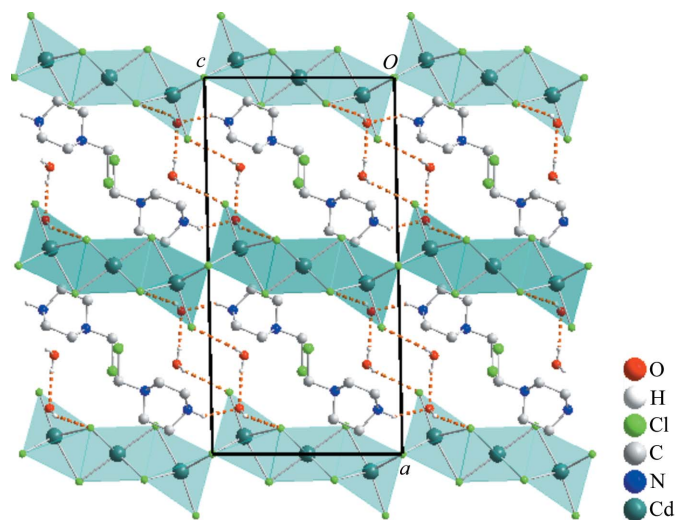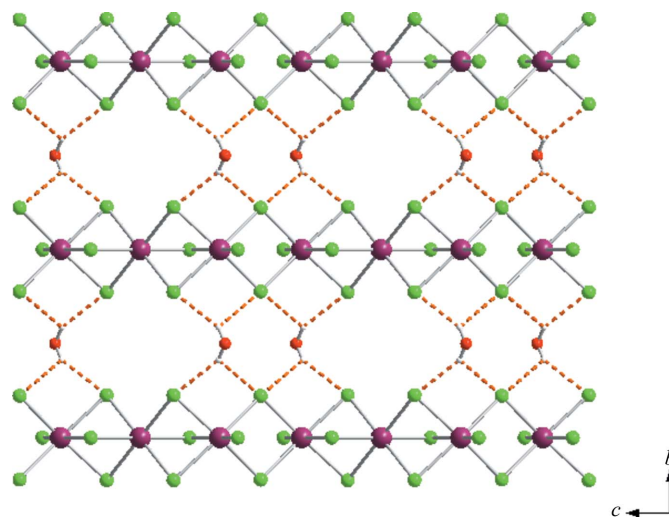
Figure 2
A view of the packing of (I) along the *b* axis. The chloridocadmate chains, formed by corner-shared linear $\{[Cd_3Cl_{10}]^{4-}\}_\infty$ trimers running along the *c* axis, are separated by 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane dications and water molecules. Dashed lines indicate hydrogen bonds. H atoms bonded to C atoms have been omitted for clarity.

Figure 3
A view of the packing of (I), along the *a* axis. Dashed lines indicate hydrogen bonds. The organic dications and the O2 water molecules have been omitted for clarity.

The presence of organic cations (generally protonated amines) and solvent molecules, as spacers between the inorganic anions, can modulate the distances between chains or layers and give rise to distinctive hydrogen-bonding features and structural packings. In (I), the chains run along the *c* axis and are well separated by 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane dications and water molecules, and there is a rich network of intermolecular hydrogen-bonding interactions. The $O1-H1C\cdots Cl3^{ii}$ [symmetry code: (ii) $-x + \frac{3}{2}$, $-y + \frac{1}{2}$, $-z + 2$] hydrogen bonds between the uncoordinated water molecules and the bridging chloride anions of the inorganic chains contribute to the formation of two-dimensional supramolecular anionic layers in the *bc* plane (Fig. 3). Between adjacent anionic layers, the organic cations and water molecules pack with an ABA' sequence as a multilayer structure along the *b* axis. The *A* and *A'* layers are composed of organic cations, while the *B* layer is composed of water molecules. The $N2-H2B\cdots O1$ hydrogen bonds between 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane dications and water molecules make the chloromethyl tails of the organic cations between the *A* and *A'* layers orient face-to-face, contributing to the stability of the crystal packing. $O2-H2C\cdots Cl4$ and $O2-H2D\cdots O1$ hydrogen bonds to terminal chlorides in adjacent anionic layers and to water molecules, respectively, generate a three-dimensional network.

In (I), the 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane cation is ordered, as indicated by the $N-C-C-N$ torsion angles. By contrast, the 1,4-diazoniabicyclo[2.2.2]octane cation is found to be disordered in several cases, including the 1:1 salts with perchloric acid (Katrusiak, 2000), trichromate (Ding *et al.*, 2004), biphenol (Ferguson *et al.*, 1998) and fluoroborate (Budzianowski *et al.*, 2008).

Our interest in chloridocadmate complexes rests on their potential as molecule-based ferroelectrics. Temperature-dependent dielectric constant measurements were performed on a powder sample in order to see whether (I) is a ferroelectric (Ye *et al.*, 2006; Fu *et al.*, 2007; Zhao *et al.* 2008; Zhang *et al.*, 2008; Ye *et al.* 2009). Unfortunately, the compound has no dielectric anomalies in the temperature range 93–353 K, suggesting that it might be only a paraelectric.

Experimental

1,4-Diazabicyclo[2.2.2]octane (5.6 g, 0.05 mol) was added to dichloromethane (20 ml) and the mixture was refluxed for 8 h. On standing for about 16 h at room temperature, a white precipitate of 1-chloromethyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride was obtained. The title compound was synthesized by adding a solution of 1-chloromethyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (1.97 g, 10 mmol) in HCl (37%, 20 ml) to a solution of cadmium chloride (1.826 g, 8 mmol) in H_2O (20 ml). After a few weeks, colourless hygroscopic prism-shaped crystals of (I) were obtained on slow evaporation of the solvent.

Crystal data

$(C_7H_{15}ClN_2)_2[Cd_3Cl_{10}]\cdot 4H_2O$	$V = 1644.1 (16)$ Å^3
$M_r = 1089.08$	$Z = 2$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 20.218 (14)$ Å	$\mu = 2.93$ mm^{-1}
$b = 7.968 (4)$ Å	$T = 293$ K
$c = 10.208 (5)$ Å	$0.30 \times 0.25 \times 0.20$ mm
$\beta = 91.288 (13)°$	

Data collection

Rigaku Mercury2 diffractometer	8541 measured reflections
Absorption correction: multi-scan	1975 independent reflections
(*CrystalClear*; Rigaku, 2005)	1830 reflections with $I > 2\sigma(I)$
$T_{min} = 0.420$, $T_{max} = 0.560$	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	103 parameters
$wR(F^2) = 0.085$	H-atom parameters constrained
$S = 1.30$	$\Delta\rho_{max} = 0.80$ e Å^{-3}
1975 reflections	$\Delta\rho_{min} = -0.99$ e Å^{-3}

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Table 1
Selected bond lengths (Å).

Cd1—Cl2	2.5471 (15)	Cd2—Cl5	2.6364 (11)
Cd1—Cl3	2.6940 (12)	Cd2—Cl3	2.6914 (12)
Cd2—Cl4	2.506 (2)	Cd2—Cl2^i	2.7771 (19)

Symmetry code: (i) $-x + 1, -y, -z + 3$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$C\cdots$Cl3^{ii}	0.85	2.52	3.283 (3)	150
O2—H2$D\cdots$O1	0.85	2.00	2.851 (7)	173
O2—H2$C\cdots$Cl4	0.85	2.81	3.201 (6)	110
N2—H2$B\cdots$O1	0.91	1.98	2.769 (5)	144

Symmetry code: (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 2$.

Considering the difficulty of finding H atoms in a difference Fourier map derived from room-temperature data in a crystal containing heavy atoms such as Cd, all H atoms were generated geometrically and refined using a riding model, with N—H = 0.90 Å, C—H = 0.96 Å or O—H = 0.85 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(O).

H atoms bonded to O atoms were generated according to the possible directions of the hydrogen bonds, as well as the supposition of sp^3 hybridization of the O atoms. First of all, atom O1 is the acceptor in an N—H$\cdots$O hydrogen bond. Geometric analysis shows that hydrogen bonds may also form between O atoms, and between O and Cl atoms. For the hydrogen bond between atoms O1 and O2, not enough structural information can be obtained to determine which is the donor and which the acceptor, and therefore one possibility was chosen. Three H atoms were generated on O1 by linking atoms N2 and O1, and then the command HADD 3 in the *XP* program (Sheldrick, 2008) was used so that atom O1 has a tetrahedral geometry. One of the three H atoms is located on a special position (mirror) and this O—H bond points to atom O2, while the other two are mirror symmetry related and may be involved in the O—H$\cdots$Cl hydrogen bond. Similarly, four H atoms bonded to atom O2 can be generated. One is located on the mirror and the O—H bond points to atom O1, two are mirror related and may be involved in O—H$\cdots$Cl hydrogen bonds, and the last one cannot be involved in any hydrogen bond so was omitted. To maintain a sensible geometry, one of the two neighbouring H atoms in the mirror has to be omitted, so we omitted that bonded to atom O1.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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