catena-Poly[[aquacadmium(II)]-bis(μ₂-4-chlorobenzoato)]

Chong-Qing Wan,* Zi-Jia Wang and Fan Zhang

Department of Chemistry, Capital Normal University, Beijing 100048, People's Republic of China

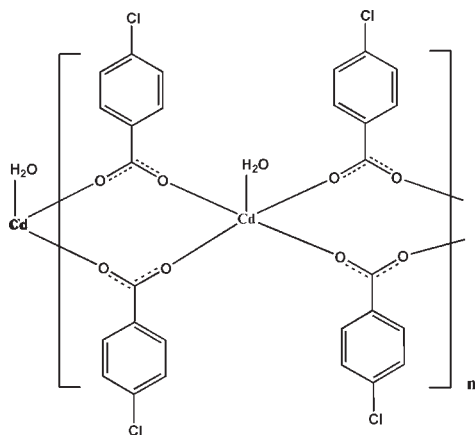Correspondence e-mail: wanchqing@yahoo.com.cn

In the title complex, $[Cd(C_7H_4ClO_2)_2(H_2O)]_n$, the Cd atom lies on a twofold axis and adopts a square-pyramidal coordination geometry. The water molecule occupies the axial site with O atoms from four different 4-chlorobenzoato ligands in the equatorial plane. Pairs of 4-chlorobenzoato ligands bridge adjacent Cd^{II} ions, generating an infinite chain structure along the c axis. Parallel polymeric chains are further interconnected through water–acetate O—H···O hydrogen bonds, forming layers in the bc plane.

Related literature

For the use of organic acids in constructing metal-organic frameworks, see: Zhao *et al.* (2003); Cao *et al.* (2002); Zhang *et al.* (2004). The related six-coordinate Cd^{II} complex with two coordinated water molecules has a distorted octahedral geometry, see: Rodesiler *et al.* (1985). For other related structures involving the 4-chlorobenzoato anion, see: Turpeinen *et al.* (1999); Xue *et al.* (2006).

Experimental

Crystal data

$[Cd(C_7H_4ClO_2)_2(H_2O)]$	$V = 1486.48$ (19) Å³
$M_r = 441.52$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 32.525$ (2) Å	$\mu = 1.85$ mm⁻¹
$b = 6.4769$ (5) Å	$T = 296$ K
$c = 7.1419$ (6) Å	$0.4 \times 0.3 \times 0.2$ mm
$\beta = 98.883$ (3)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	9459 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	1334 independent reflections
$T_{min} = 0.567$, $T_{max} = 0.746$	1308 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	101 parameters
$wR(F^2) = 0.042$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{max} = 0.26$ e Å⁻³
1334 reflections	$\Delta\rho_{min} = -0.34$ e Å⁻³

Table 1
Selected bond lengths (Å).

Cd1—O1ⁱ	2.2210 (14)	Cd1—O2ⁱⁱ	2.3896 (14)
Cd1—O1W	2.233 (2)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O2ⁱⁱⁱ	0.89	1.88	2.699 (2)	153

Symmetry code: (iii) $x, y - 1, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* and *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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metal-organic compounds

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supporting information

catena-Poly[[aquacadmium(II)]-bis(*μ*₂-4-chlorobenzoato)]

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S1. Comment

Organic acids are widely used as versatile building blocks in many metal- organic frameworks with diverse structural motifs (Zhao *et al.*, 2003; Cao *et al.*, 2002; Zhang *et al.*, 2004). In metal complexes the 4-chlorobenzoato anion can function both to balance charge and as a bridging ligand. Several structures incorporating this ligand have been investigated (Turpeinen, *et al.*, 1999; Xue *et al.*, 2006).
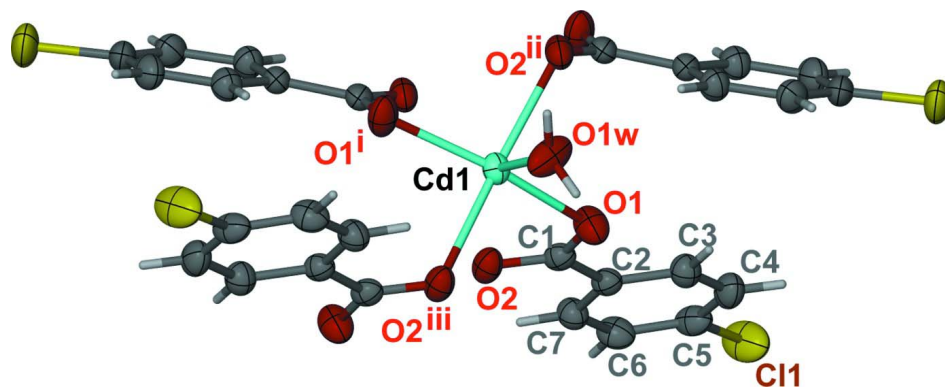
Herein we report a new compound $[Cd(C_7H_4ClO_2)_2.H_2O]_\infty$ derived from 4-chlorobenzoic acid, which exhibits an one-dimensional infinite chain structure. In the title complex the Cd^{II} atom lies on a two-fold axis and adopts a square pyramidal coordination geometry (Fig. 1). The water molecule occupies the axial site with oxygen atoms from four different 4-chlorobenzoato ligands in the equatorial plane. The Cd—O1W bond length is 2.233 (2)Å and the Cd—*O*(acetate) distances lie in the range 2.221 (1)-2.390 (1) Å, Table 1. Pairs of 4-chlorobenzoato ligands bridge two adjacent Cd^{II} ions generating an infinite chain structure along the *c* axis. Parallel polymeric chains are further interconnected through O1W—H1WA···O2 hydrogen bonds forming layers in the *bc* plane (Fig. 2, Table 2), with an O1W···O2 (D···A) distance of 2.699 (2) Å. This structure is entirely different from that of $[Cd(C_7H_4ClO_2)_2.(H_2O)_2]$, in which the Cd^{II} ion adopts a distorted six-coordination geometry (Rodesiler *et al.*, 1985).

S2. Experimental

4-chlorobenzoic acid (0.040 g, 0.3 mmol) was dissolved in a mixture of methanol, 2 ml, and acetonitrile, 2 ml. Sodium hydroxide was subsequently added at room temperature to adjust the pH to 7. Then, $Cd(ClO_4)_2.6H_2O$ (0.371 g, 0.1 mmol) was added and the solution stirred for an hour. The clear solution was filtered and then left to stand in air. After 6 days colorless rod-like crystals were deposited (260 mg, 72% yield).

S3. Refinement

The hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms, with C— H = 0.93 Å and *U*ĩso~(H) = 1.2Ueq(C). The position of the hydrogen atom of the coordinated water molecule was obtained from a difference Fourier map, with the O—H distances restrained to 0.89 Å.

Figure 1

The structure of (I) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as rods of arbitrary radius. [Symmetry Codes: (i) –x, y, –z + 1/2; (ii) –x, –y, –z + 1; (iii) x, –y, z – 1/2]

Figure 2

Hydrogen-bonding interactions (dashed lines) between parallel chains along the *c* axis of complex (I).

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Crystal data

[Cd(C₇H₄ClO₂)₂(H₂O)]
$M_r = 441.52$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 32.525$ (2) Å
$b = 6.4769$ (5) Å
$c = 7.1419$ (6) Å
$\beta = 98.883$ (3)°
$V = 1486.48$ (19) Å³
$Z = 4$

$F(000) = 864$
$D_x = 1.973$ Mg m⁻³
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 543 reflections
$\theta = 2.3–26.7°$
$\mu = 1.85$ mm⁻¹
$T = 296$ K
Rod, colorless
$0.4 \times 0.3 \times 0.2$ mm

Data collection

Bruker APEXII CCD area-detector
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan
    (*SADABS*; Bruker, 2007)
$T_{min} = 0.567$, $T_{max} = 0.746$

9459 measured reflections
1334 independent reflections
1308 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.1°$, $\theta_{min} = 3.2°$
$h = -38 \rightarrow 38$
$k = -7 \rightarrow 7$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.042$
$S = 1.12$
1334 reflections
101 parameters
0 restraints
Primary atom site location: structure-invariant
    direct methods

Secondary atom site location: difference Fourier
    map
Hydrogen site location: inferred from
    neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 1.3036P]$ $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å⁻³
$\Delta\rho_{min} = -0.34$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cd1	0.0000	−0.15461 (2)	0.2500	0.02841 (8)
Cl1	0.222718 (19)	0.55886 (13)	0.63416 (9)	0.0652 (2)
O1	0.06477 (4)	−0.0960 (2)	0.3902 (2)	0.0444 (3)

O2	0.02952 (4)	0.1741 (2)	0.4642 (2)	0.0361 (3)
C1	0.06390 (6)	0.0837 (3)	0.4530 (2)	0.0306 (4)
C2	0.10373 (6)	0.1976 (3)	0.5081 (2)	0.0298 (4)
C3	0.10333 (6)	0.4005 (3)	0.5697 (3)	0.0355 (4)
H3A	0.0782	0.4630	0.5836	0.043*
C4	0.14008 (6)	0.5103 (3)	0.6107 (3)	0.0405 (5)
H4A	0.1398	0.6468	0.6510	0.049*
C5	0.17716 (6)	0.4147 (4)	0.5911 (3)	0.0407 (5)
C6	0.17853 (6)	0.2115 (4)	0.5343 (3)	0.0421 (5)
H6A	0.2038	0.1485	0.5249	0.050*
C7	0.14156 (6)	0.1033 (3)	0.4914 (3)	0.0363 (4)
H7A	0.1420	−0.0332	0.4513	0.044*
O1W	0.0000	−0.4993 (3)	0.2500	0.0527 (6)
H1WA	0.0106	−0.5756	0.3494	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02668 (12)	0.02429 (12)	0.03493 (12)	0.000	0.00687 (8)	0.000
Cl1	0.0426 (3)	0.0929 (5)	0.0609 (4)	−0.0347 (3)	0.0102 (3)	−0.0183 (3)
O1	0.0365 (8)	0.0428 (8)	0.0546 (9)	−0.0097 (6)	0.0093 (6)	−0.0179 (7)
O2	0.0272 (7)	0.0388 (7)	0.0420 (8)	−0.0023 (5)	0.0047 (6)	0.0094 (5)
C1	0.0300 (9)	0.0369 (10)	0.0252 (8)	−0.0059 (8)	0.0047 (7)	0.0034 (7)
C2	0.0282 (9)	0.0356 (9)	0.0260 (8)	−0.0046 (7)	0.0047 (7)	0.0006 (7)
C3	0.0316 (10)	0.0396 (10)	0.0360 (9)	−0.0026 (8)	0.0075 (8)	−0.0046 (8)
C4	0.0434 (11)	0.0411 (11)	0.0377 (10)	−0.0117 (9)	0.0081 (8)	−0.0080 (8)
C5	0.0323 (10)	0.0579 (13)	0.0315 (9)	−0.0160 (9)	0.0036 (8)	−0.0014 (9)
C6	0.0273 (10)	0.0556 (12)	0.0434 (11)	0.0006 (9)	0.0055 (8)	0.0032 (10)
C7	0.0328 (10)	0.0374 (10)	0.0390 (10)	0.0000 (8)	0.0069 (8)	0.0016 (8)
O1W	0.0701 (15)	0.0225 (10)	0.0564 (13)	0.000	−0.0190 (11)	0.000

Geometric parameters (Å, º)

Cd1—O1^i	2.2210 (14)	C2—C7	1.395 (3)
Cd1—O1	2.2210 (14)	C3—C4	1.383 (3)
Cd1—O1W	2.233 (2)	C3—H3A	0.9300
Cd1—O2^{ii}	2.3896 (14)	C4—C5	1.382 (3)
Cd1—O2^{iii}	2.3896 (14)	C4—H4A	0.9300
Cl1—C5	1.738 (2)	C5—C6	1.380 (3)
O1—C1	1.249 (2)	C6—C7	1.385 (3)
O2—C1	1.276 (2)	C6—H6A	0.9300
O2—Cd1^{iii}	2.3896 (14)	C7—H7A	0.9300
C1—C2	1.490 (3)	O1W—H1WA	0.8900
C2—C3	1.386 (3)		
O1^i—Cd1—O1	160.33 (8)	C7—C2—C1	120.18 (18)
O1^i—Cd1—O1W	99.84 (4)	C4—C3—C2	120.30 (18)
O1—Cd1—O1W	99.84 (4)	C4—C3—H3A	119.9

O1ⁱ—Cd1—O2ⁱⁱ	95.88 (5)	C2—C3—H3A	119.9
O1—Cd1—O2ⁱⁱ	85.16 (5)	C5—C4—C3	119.15 (19)
O1W—Cd1—O2ⁱⁱ	86.97 (3)	C5—C4—H4A	120.4
O1ⁱ—Cd1—O2ⁱⁱⁱ	85.16 (5)	C3—C4—H4A	120.4
O1—Cd1—O2ⁱⁱⁱ	95.88 (5)	C6—C5—C4	121.72 (18)
O1W—Cd1—O2ⁱⁱⁱ	86.97 (3)	C6—C5—Cl1	119.92 (16)
O2ⁱⁱ—Cd1—O2ⁱⁱⁱ	173.94 (6)	C4—C5—Cl1	118.34 (17)
C1—O1—Cd1	104.39 (12)	C5—C6—C7	118.77 (19)
C1—O2—Cd1ⁱⁱⁱ	120.07 (11)	C5—C6—H6A	120.6
O1—C1—O2	121.26 (17)	C7—C6—H6A	120.6
O1—C1—C2	119.30 (17)	C6—C7—C2	120.4 (2)
O2—C1—C2	119.39 (17)	C6—C7—H7A	119.8
C3—C2—C7	119.59 (18)	C2—C7—H7A	119.8
C3—C2—C1	120.18 (17)	Cd1—O1W—H1WA	123.7
O1ⁱ—Cd1—O1—C1	21.30 (11)	O2—C1—C2—C7	−178.09 (17)
O1W—Cd1—O1—C1	−158.70 (11)	C7—C2—C3—C4	1.4 (3)
O2ⁱⁱ—Cd1—O1—C1	115.23 (12)	C1—C2—C3—C4	−176.33 (18)
O2ⁱⁱⁱ—Cd1—O1—C1	−70.77 (12)	C2—C3—C4—C5	−0.6 (3)
Cd1—O1—C1—O2	14.4 (2)	C3—C4—C5—C6	−0.9 (3)
Cd1—O1—C1—C2	−162.92 (13)	C3—C4—C5—Cl1	177.43 (16)
Cd1ⁱⁱⁱ—O2—C1—O1	92.47 (18)	C4—C5—C6—C7	1.6 (3)
Cd1ⁱⁱⁱ—O2—C1—C2	−90.19 (17)	Cl1—C5—C6—C7	−176.69 (16)
O1—C1—C2—C3	176.98 (18)	C5—C6—C7—C2	−0.8 (3)
O2—C1—C2—C3	−0.4 (3)	C3—C2—C7—C6	−0.6 (3)
O1—C1—C2—C7	−0.7 (3)	C1—C2—C7—C6	177.07 (18)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2; (ii) *x*, −*y*, *z*−1/2; (iii) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O2ⁱᵛ	0.89	1.88	2.699 (2)	153

Symmetry code: (iv) *x*, *y*−1, *z*.