Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[[[aquabis(1*H*-benzimidazole-κN^3)cadmium(II)]-μ-phthalato-$\kappa^3 O,O':O''$] hemihydrate]

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Received 20 January 2004
Accepted 9 March 2004
Online 31 March 2004

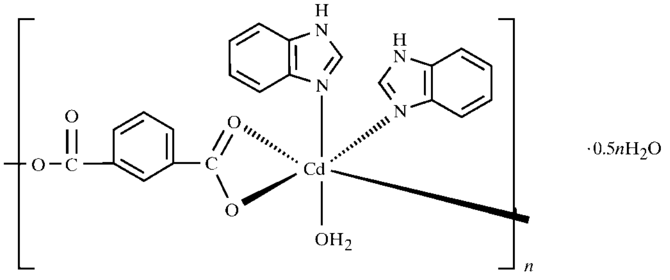
The title compound is a polymeric complex bridged by a phthalate dianion, $\{[Cd(C_8H_4O_4)(C_7H_6N_2)_2(H_2O)]\cdot 0.5H_2O\}_n$. The asymmetric unit contains two Cd complex units, and both Cd^{II} atoms have the same distorted octahedral coordination geometry. Each phthalate dianion bridges two Cd atoms through the two terminal carboxy groups, one in a monodentate fashion and the other in a chelating mode, thus forming zigzag polymeric chains; π–π stacking occurs between neighboring chains. The bond angle involving the chelating carboxy group is large, but the corresponding bond distance is normal. This implies the existence of an electrostatic interaction between the Cd^{II} atoms and the carboxy groups.

Comment

The consequences of non-covalent interactions in chemistry and structural biology have stimulated interest in exploring a variety of intermolecular forces. The aromatic π–π stacking interaction is correlated with electron transfer in some biological systems (Deisenhofer & Michel, 1989), and several structure determinations have revealed that the π–π stacking interaction commonly occurs in metal complexes with aromatic heteropolycyclic ligands (Nie *et al.*, 2001). We present here the structure of the polymeric Cd^{II} complex, (I), of benzimidazole, in which π–π stacking occurs between adjacent polymeric chains.

The asymmetric unit of (I) contains two complex Cd^{II} units and one lattice water molecule, as shown in Fig. 1. The two independent Cd atoms have the same distorted octahedral coordination geometry, formed by two benzimidazole groups (BZIM) in a *cis* configuration, a coordinated water molecule and two phthalate dianions. Each phthalate dianion coordinates to two independent Cd atoms through the two terminal carboxy groups, one in a monodentate fashion and the other in a chelating mode.

In the Cd1 complex unit, the O2—Cd1—N13 and O2—Cd1—$O9^{i}$ angles [symmetry code: (i) $x - 1, y, 1 + z$; Table 1] are close to expected values, implying significant overlap of the Cd1 and O2 atomic orbitals, whereas the O1—Cd1—$O9^{i}$ angle [122.66 (7)°] suggests little overlap of the Cd1 and O1 atomic orbitals. However, the Cd1—O1 bond distance is essentially the same as the Cd1—O2 bond distance. Likewise, in the Cd2 complex unit, the O6—Cd2—N43 and O6—Cd2—O3 angles imply significant overlap of the Cd2 and O6 atomic orbitals, whereas the O7—Cd2—O3 angle [119.72 (7)°] suggests little overlap of the Cd2 and O7 atomic orbitals. However, the Cd2—O7 bond is shorter than the Cd2—O6 bond. These facts imply the existence of an electrostatic interaction between the Cd atom and the coordinated carboxy group.



(I)

The Cd1—$O9^{i}$ and Cd2—O3 bonds for the monodentate carboxy groups are significantly shorter than the chelating Cd—O bonds. Uncoordinated carboxy atoms O4 and O8 are hydrogen bonded to the neighboring coordinated water molecules O10 and O5. In addition, lattice water molecules O1*W* and O1W^{ii} hydrogen bond with carboxy groups bonded to the Cd2 complex unit (Fig. 1), but there are no lattice water interactions with carboxy groups bonded to the Cd1 complex unit. Thus, the Cd1 and Cd2 complex units are different.

Carboxy atoms O1, O2 and $O9^{i}$, and BZIM atom N13 form an equatorial coordination plane around atom Cd1, with a maximum atomic deviation of 0.0339 (10) Å (for O2), while atoms O6, O7, O3 and N43 form another equatorial coordination plane around atom Cd2, with a maximum atomic deviation of 0.0759 (12) Å (for O6). The plane of the C31 phthalate dianion bridging the two Cd complex units is nearly parallel to both equatorial planes, the dihedral angles being 4.71 (11) and 2.71 (11)°. Thus, the two equatorial coordinate planes are also nearly parallel, the dihedral angle being 3.80 (14)°.

Phthalate dianions bridge the adjacent Cd atoms to form zigzag polymeric chains, as shown in Fig. 2, along the $[10\bar{1}]$ direction; π–π stacking interactions occur between neighboring polymeric chains related by an inversion center. The parallel N43-BZIM and $N43^{iv}$-BZIM rings [symmetry code: (iv) $1 - x, 1 - y, 1 - z$] overlap one another, as do the parallel C62-phthalate and $C62^{vi}$-phthalate rings [symmetry code: (vi) $2 - x, 1 - y, -z$], as shown in Fig. 2. The separations between the neighboring parallel aromatic rings are 3.427 (14) (BZIM rings) and 3.298 (19) Å (phthalate rings).

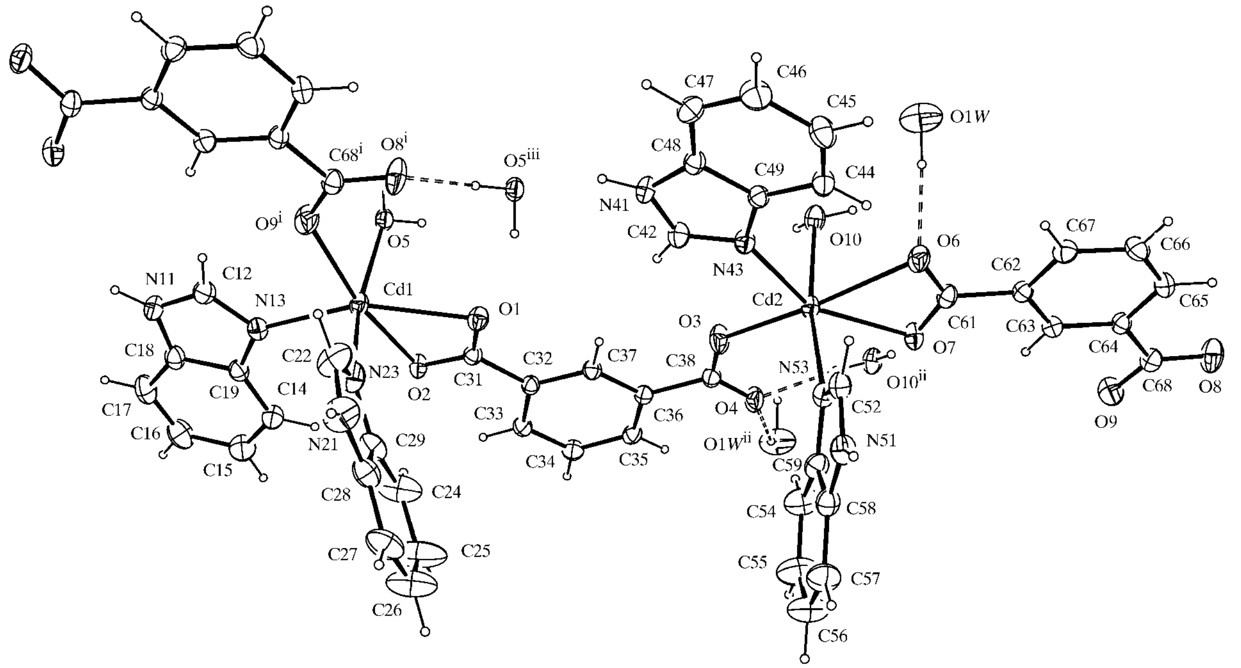


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $x - 1, y, 1 + z$; (ii) $1 - x, 1 - y, -z$; (iii) $-x, 1 - y, 1 - z$.]

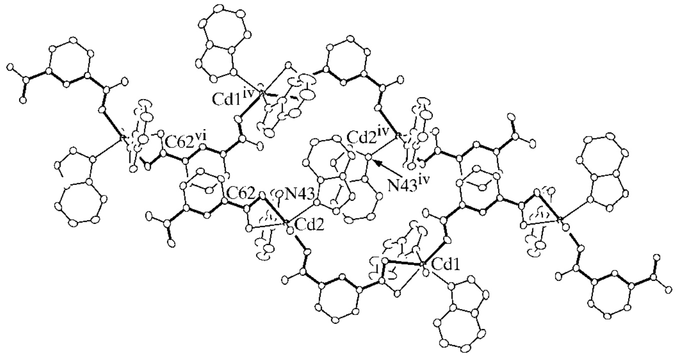


Figure 2
The zigzag polymeric chains and the overlapped arrangement of aromatic rings of adjacent chains. [Symmetry codes: (iv) $1 - x, 1 - y, 1 - z$; (vi) $2 - x, 1 - y, -z$.]

Besides the hydrogen bonding between the carboxy and water O atoms mentioned above, hydrogen bonding is also observed between the BZIM and water molecules, and between the BZIM and carboxy groups (Table 2).

Experimental

An aqueous solution (20 ml) of benzimidazole (0.12 g, 1 mmol) and $CdCl_2 \cdot 2H_2O$ (0.22 g, 1 mmol) was mixed with an aqueous solution (15 ml) of phthalic acid (0.17 g, 1 mmol) and NaOH (0.08 g, 2 mmol) at room temperature. The mixture was refluxed for 3 h and filtered twice. Single crystals were obtained from the filtrate after four weeks.

Crystal data

$[Cd(C_8H_4O_4)(C_7H_6N_2)_2(H_2O)] \cdot 0.5H_2O$
$M_r = 1079.62$
Triclinic, $P\overline{1}$
$a = 12.2779$ (12) Å
$b = 13.9092$ (12) Å
$c = 14.2565$ (13) Å
$\alpha = 61.1400$ (10)°
$\beta = 80.629$ (2)°
$\gamma = 88.4640$ (10)°
$V = 2100.1$ (3) Å^3
$Z = 2$
$D_x = 1.707$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7404 reflections
$\theta = 1.7$–25.1°
$\mu = 1.09$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.32 × 0.21 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.702$, $T_{max} = 0.895$
16 098 measured reflections
7404 independent reflections
6572 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.2$°
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.060$
$S = 1.07$
7404 reflections
586 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 1.7003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

H atoms on water molecules were located in a difference Fourier map and were included with fixed positional and isotropic displacement parameters [$U_{iso}(H) = 0.05$ Å^2]. Other H atoms were placed in calculated positions (C—H = 0.93 Å and N—H = 0.86 Å) and were

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.4083 (17)	Cd2—O3	2.2028 (17)
Cd1—O2	2.3774 (17)	Cd2—O6	2.3950 (19)
Cd1—O5	2.4255 (18)	Cd2—O7	2.3511 (17)
Cd1—O9^{i}	2.2203 (19)	Cd2—O10	2.4471 (19)
Cd1—N13	2.292 (2)	Cd2—N43	2.273 (2)
Cd1—N23	2.306 (2)	Cd2—N53	2.311 (2)
O1—Cd1—O2	54.72 (6)	O3—Cd2—O6	168.42 (7)
O1—Cd1—O9^{i}	122.66 (7)	O3—Cd2—O7	119.72 (7)
O1—Cd1—N13	150.05 (7)	O3—Cd2—N43	88.68 (7)
O2—Cd1—O9^{i}	164.37 (8)	O6—Cd2—O7	55.21 (6)
O2—Cd1—N13	95.42 (7)	O6—Cd2—N43	95.52 (7)
O9^{i}—Cd1—N13	86.59 (8)	O7—Cd2—N43	150.69 (7)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O6	0.96	1.86	2.804 (4)	169
O1W—H1B···O4^{ii}	0.93	2.14	3.010 (4)	156
O5—H5A···O8^{ii}	0.84	1.84	2.660 (3)	168
O5—H5B···O1^{iii}	0.97	1.93	2.836 (3)	155
O10—H10A···O7^{ii}	0.87	1.89	2.745 (3)	166
O10—H10B···O4^{ii}	0.86	1.92	2.776 (3)	173
N11—H11···O10^{iii}	0.86	2.34	3.020 (4)	136
N21—H21···O1W^{iv}	0.86	2.15	2.899 (4)	145
N41—H41···O5^{iii}	0.86	2.17	2.907 (3)	143
N51—H51···O2^{v}	0.86	2.07	2.915 (3)	170

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

included in the final cycles of refinement in riding mode, with $U_{\rm iso}$(H) values set equal to 1.2$U_{\rm eq}$ of the bonded atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the Analytical Foundation of Zhejiang University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1465). Services for accessing these data are described at the back of the journal.

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