metal-organic compounds

Acta Crystallographica Section C Crystal Structure Communications ISSN 0108-2701

trans-Dichlorotetrabenzimidazolecadmium(II) tetrabenzimidazole: a three-dimensional supramolecular structure built from C— $H \cdots \pi$, N— $H \cdots CI$ and N— $H \cdots N$ hydrogen bonds

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Received 14 February 2006 Accepted 9 March 2006 Online 13 April 2006

The title compound, $[CdCl_2(C_7H_6N_2)_4]\cdot 4C_7H_6N_2$, consists of a $Cd(Bzim)_4Cl_2$ complex (Bzim is benzimidazole) lying on a fourfold rotation axis in the space group *P4nc*, and four benzimidazole molecules which are linked to the coordinated benzimidazole unit by $N-H\cdots N$ hydrogen bonds. One $N-H\cdots Cl$ and three $C-H\cdots \pi$ hydrogen bonds link these units into a three-dimensional supramolecular structure.

Comment

Benzimidazole is a very important group which has been applied in the drug design of antitumour agents (Arrowsmith *et al.*, 2002; Hay *et al.*, 2003), and its metal complexes are reported to have the activities of the superoxide dismutase (SOD) (Nishida *et al.*, 1991; Kwak *et al.*, 1999; Liao *et al.*, 2001; Qin *et al.*, 2005) and nuclease (Liu *et al.*, 2004) enzymes. Because of our interest in these areas, the title compound, (I), was synthesized and we report its crystal structure here.

Compound (I) (Fig. 1) consists of a $Cd(Bzim)_4Cl_2$ complex and four free benzimidazole (Bzim) molecules, lying around a fourfold rotation axis in the space group *P4nc*. In the complex, four N atoms from four benzimidazole ligands and two Cl⁻ counter-anions coordinate to Cd^{2+} , giving rise to an octahedron with four N atoms in the equatorial plane and two Cl⁻ anions occupying the apical positions. It is interesting that the four benzimidazole ligands coordinated to Cd surround the Cd atom like a flower, similar to the structure in the complex $[Ni_2Cl_3(Bzim)_8]Cl\cdot4C_3H_6O$ (Drew *et al.*, 1968). Each benzimidazole ligand is inclined to the equatorial plane of the octahedron at an angle of 41.19 (6)°. Associated with the asymmetric arrangement of benzimidazole ligands along the axial direction, the two Cd—Cl1 distances differ significantly (Table 1). The four free benzimidazole molecules are hydrogen bonded to the four coordinated benzimidazole ligands by N2-H···N3 bonding, with a dihedral angle between the hydrogen-bonded benzimidazole ligands of 82.69 (8)°. Therefore, the whole structure of (I) is like a flower with double-layer foliage, forming a fourfold axially symmetric molecule.



Three $C-H\cdots\pi$ and one $N-H\cdots$ Cl hydrogen bond (Table 2) link the complexes into ladders along [001]. The two $C-H\cdots\pi$ interactions $C1-H\cdots Cg1^{ii}$ [*Cg*1 is the centroid of the C9–C14 ring; symmetry code: (ii) $\frac{3}{2} - y$, $\frac{3}{2} - x$, $\frac{1}{2} + z$] and $C8-H\cdots Cg2^{ii}$ (*Cg*2 is the centroid of the C2–C7 ring) link neighbouring hydrogen-bonded benimidazole pairs to form a zigzag double chain in the *c* direction. The third $C-H\cdots\pi$ interaction is between C6–H and the centroid of the fivemembered ring N3/C8/N4/C10/C9 at the symmetry position $(\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$. All hydrogen bonds involve the uncoor-





The structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii and dotted lines indicate hydrogen bonds. [Symmetry codes: (i) 1 - x, 1 - y, z; (ii) 1 - y, x, z; (iii) y, 1 - x, z.]



Figure 2

The edge-to-face $C-H \cdots \pi$ (dashed lines) and $N-H \cdots Cl$ (dotted lines) hydrogen bonding in (I). H atoms not involved the hydrogen bonding shown in the figure have been omitted for clarity. *Cg*₁ is the centroid of the C9–C14 ring, *Cg*₂ is the centroid of the C2–C7 ring and *Cg*₃ is the centroid of the N3/ C8/N4/C10/C9 ring. [Symmetry codes: (i) 1 - y, x, z; (ii) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; (iii) y, 1 - x, -1 + z; (iv) $\frac{1}{2} - y$, $\frac{3}{2} - x$, $-\frac{1}{2} + z$.]

dinated benzimidazole. Therefore, in the crystal structure of compound (I), the free benzimidazoles are actually stabilized outside the complex by five hydrogen bonds. As the complex is a fourfold axially symmetric molecule and neighbouring molecules have the same interactions in four directions, so every molecule of (I) indeed connects eight neighbouring ones at the apical positions of a cube, building the compound into a three-dimensional structure.

Compared with another space group $(I4_1/a)$ of the same crystal system (Glidewell *et al.*, 2005), similar large void spaces were examined using *PLATON* (Spek, 2003). In the threedimensional structure of (I), there are channels parallel to [001] (Fig. 3) and these account in total for 193.1 Å³ per unit



Figure 3

An ab projection of the crystal structure of (I), showing the [001] channels.

cell, *i.e.* some 7.1% of the total volume. The channels lie along the twofold axes, with an average cross-sectional area of *ca* 10.4 Å² and an average diameter of *ca* 3.64 Å. The reflection data were subjected to the SQUEEZE routine in *PLATON* before the final refinement, and this suggested the presence of only 2.2 electrons per unit cell within the voids.

Experimental

The title compound was synthesized under hydrothermal conditions. A mixture of V_2O_5 , $CdCl_2 \cdot 2.5H_2O$, 1,2-bis(1H-benz[d]imidazol-2-yl)ethane-1,2-diol, imidazole and distilled water in a 1:1:2:2:720 molar ratio was heated from 293 to 448 K over 2 h in a 25 ml stainless steel reactor with a Teflon liner, and the temperature was kept constant at 448 K for 92 h. Yellow crystals of (I) were obtained from the filtrate at room temperature over a period of several days.

Crystal data

[CdCla(CaHaNa)].]:4CaHaNa	Mo $K\alpha$ radiation
$M_r = 1128.40$	Cell parameters from 4359
Tetragonal, P4nc	reflections
a = 17.0805 (18) Å	$\theta = 2.4-25.4^{\circ}$
c = 9.2818 (15) Å	$\mu = 0.56 \text{ mm}^{-1}$
V = 2707.9 (6) Å ³	T = 298 (2) K
Z = 2	Block, yellow
$D_x = 1.384 \text{ Mg m}^{-3}$	$0.40 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Bruker SMART 1K CCD areadetector diffractometer2379 independent reflections ω scans2088 reflections with $I > 2\sigma(I)$ ω scans $R_{int} = 0.039$ Absorption correction: multi-scan $\theta_{max} = 25.0^{\circ}$ (SADABS: Sheldrick, 2000) $h = -18 \rightarrow 20$ $T_{min} = 0.808, T_{max} = 0.897$ $k = -20 \rightarrow 12$ 12444 measured reflections $l = -11 \rightarrow 10$

Refinement

 $\begin{array}{ll} \mbox{Refinement on } F^2 & w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 \\ R[F^2 > 2\sigma(F^2)] = 0.036 & w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 \\ + 0.1395P] & where \ P = (F_o^2 + 2F_c^2)/3 \\ S = 1.07 & (\Delta/\sigma)_{max} < 0.001 \\ 2379 \ reflections & \Delta\rho_{max} = 0.54 \ e^{\Delta^{-3}} \\ 172 \ parameters & \Delta\rho_{min} = -0.42 \ e^{\Delta^{-3}} \\ \mbox{H-atom parameters constrained} & Absolute \ structure: \ Flack \ (1983), \\ with \ 1086 \ Friedel \ pairs \end{array}$

Flack parameter: -0.01 (4)

Table 1

Selected geometric parameters (Å, °).

Cd1-N1 Cd1-Cl2	2.357 (2) 2.645 (3)	Cd1-Cl1	2.804 (3)
N1 ⁱ -Cd1-N1	177.13 (19)	N1-Cd1-Cl1	88.56 (10)
N1-Cd1-N1 ⁱⁱ	89.964 (5)	Cl2-Cd1-Cl1	180.000(1)
N1-Cd1-Cl2	91.44 (10)		

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

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C9–C14 ring, Cg2 is the centroid of the C2–C7 ring and Cg3 is the centroid of the N3/C8/N4/C10/C9 ring.

$D - H \cdot \cdot \cdot A$	$D-\mathrm{H}$	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdots A$
$N2-H2\cdots N3$	0.86	2.07	2.836 (4)	149
N4-H4A···Cl1 ⁱⁱⁱ	0.86	2.62	3.377 (4)	147
$C1-H1\cdots Cg1^{iv}$	0.93	2.87	3.675 (4)	146
$C8-H8\cdots Cg2^{iv}$	0.93	2.61	3.525 (5)	167
$C6-H6\cdots Cg3^{v}$	0.93	2.88	3.527 (6)	128

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

H atoms attached to C and N atoms were placed in geometrically idealized positions, with C-H = 0.93 Å and N-H = 0.86 Å, and refined with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$. The correct orientation of the structure relative to the polar-axis direction was established using the Flack (1983) parameter. Examination of the refined structure using *PLATON* (Spek, 2003) revealed the presence of void spaces having a total volume of 193.1 Å³ per unit cell, arranged into four channels along the *c*-axis direction. There was a low residual electron density of 0.54 e Å⁻³ located 0.94 Å from atom Cd1.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

The authors acknowledge the National Natural Science Foundation of China (grant No. 20471033), the Natural Science Foundation of Shanxi Province (grant No. 20051013) and the Overseas Returned Scholar Foundation of Shanxi Province for financial support. The authors also thank Dr Jean-Claude Daran (Laboratoire de Chimie de Coordination, France) for his help.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3005). Services for accessing these data are described at the back of the journal.

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