

trans-Dichlorotetrabenzimidazole-cadmium(II) tetrabenzimidazole: a three-dimensional supramolecular structure built from C—H··· π , N—H···Cl and N—H···N hydrogen bonds

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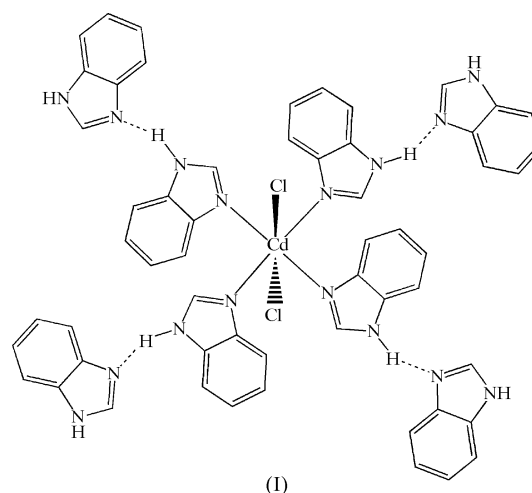
The title compound, [CdCl₂(C₇H₆N₂)₄].4C₇H₆N₂, consists of a Cd(Bzim)₄Cl₂ complex (Bzim is benzimidazole) lying on a fourfold rotation axis in the space group *P4nc*, and four benzimidazole molecules which are linked to the coordinated benzimidazole unit by N—H···N hydrogen bonds. One N—H···Cl and three C—H··· π 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)₄Cl₂ 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 Cd²⁺, 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 [Ni₂Cl₃(Bzim)₈]Cl·4C₃H₆O (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··· π and one N—H···Cl hydrogen bond (Table 2) link the complexes into ladders along [001]. The two C—H··· π interactions C1—H···Cg1ⁱⁱ [Cg1 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···Cg2ⁱⁱ (Cg2 is the centroid of the C2—C7 ring) link neighbouring hydrogen-bonded benzimidazole pairs to form a zigzag double chain in the *c* direction. The third C—H··· π interaction is between C6—H and the centroid of the five-membered 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-

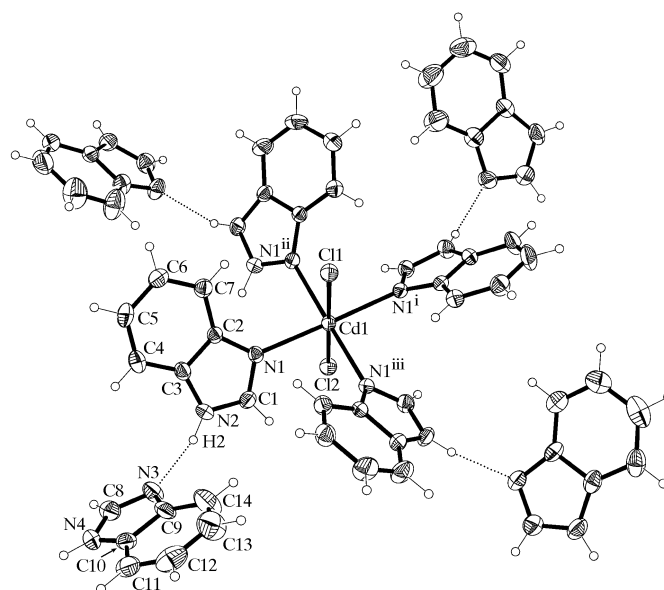


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii and dotted lines indicate hydrogen bonds. [Symmetry codes: (i) $1 - x, 1 - y, z$; (ii) $1 - y, x, z$; (iii) $y, 1 - x, z$.]

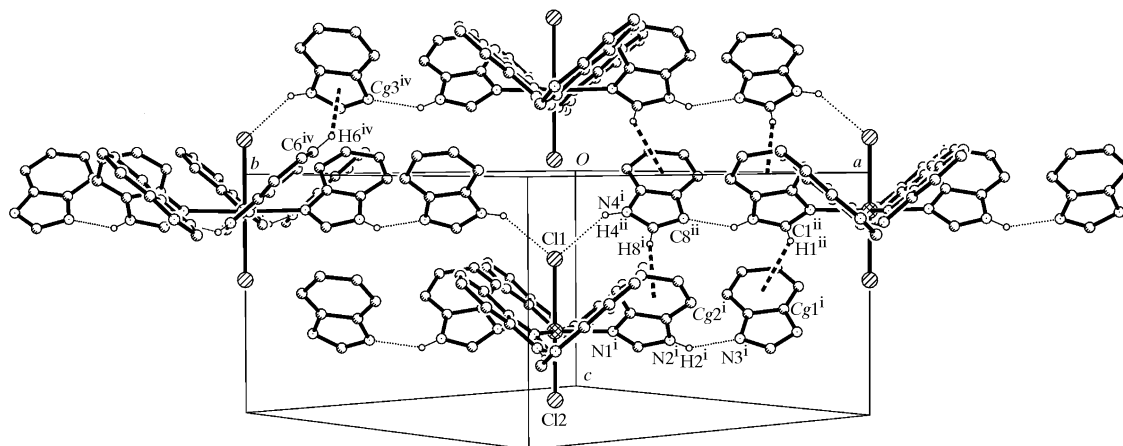


Figure 2

The edge-to-face C—H... π (dashed lines) and N—H...Cl (dotted lines) hydrogen bonding in (I). H atoms not involved in the hydrogen bonding shown in the figure have been omitted for clarity. 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. [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) $\frac{1}{2} - y, \frac{3}{2} - x, -\frac{1}{2} + z$.]

minated 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 three-dimensional structure of (I), there are channels parallel to [001] (Fig. 3) and these account in total for 193.1 Å³ per unit

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 V₂O₅, CdCl₂·2.5H₂O, 1,2-bis(1*H*-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

[CdCl₂(C₇H₆N₂)₄]·4C₇H₆N₂
M_r = 1128.40
 Tetragonal, *P4nc*
a = 17.0805 (18) Å
c = 9.2818 (15) Å
V = 2707.9 (6) Å³
Z = 2
D_x = 1.384 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 4359 reflections
 θ = 2.4–25.4°
 μ = 0.56 mm⁻¹
T = 298 (2) K
 Block, yellow
 0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
 T_{\min} = 0.808, T_{\max} = 0.897
 12444 measured reflections

2379 independent reflections
 2088 reflections with $I > 2\sigma(I)$
 R_{int} = 0.039
 θ_{max} = 25.0°
 h = -18 → 20
 k = -20 → 12
 l = -11 → 10

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.036
 $wR(F^2)$ = 0.092
 S = 1.07
 2379 reflections
 172 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1395P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 with 1086 Friedel pairs
 Flack parameter: -0.01 (4)

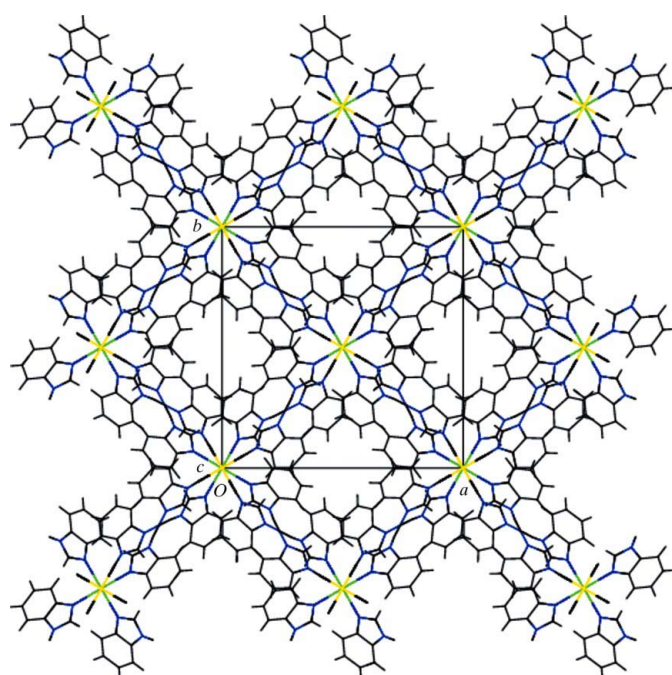


Figure 3

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

metal-organic compounds

Table 1

Selected geometric parameters (Å, °).

Cd1—N1	2.357 (2)	Cd1—Cl1	2.804 (3)
Cd1—Cl2	2.645 (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.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots N3	0.86	2.07	2.836 (4)	149
N4—H4A \cdots 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. 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*.

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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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