

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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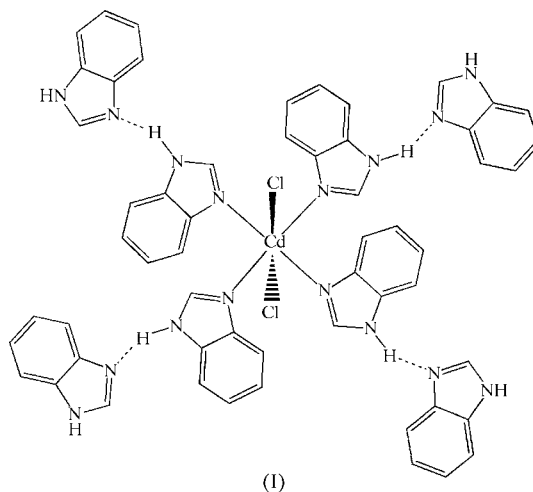
The title compound, [CdCl₂(C₇H₆N₂)₄]·4C₇H₆N₂, consists of a Cd(Bzim)₄Cl₂ complex (Bzim is benzimidazole) lying on a fourfold rotation axis in the space group *P4nc*, and four benzimidazole molecules which are linked to the coordinated benzimidazole unit by N—H···N hydrogen bonds. One N—H···Cl and three 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-

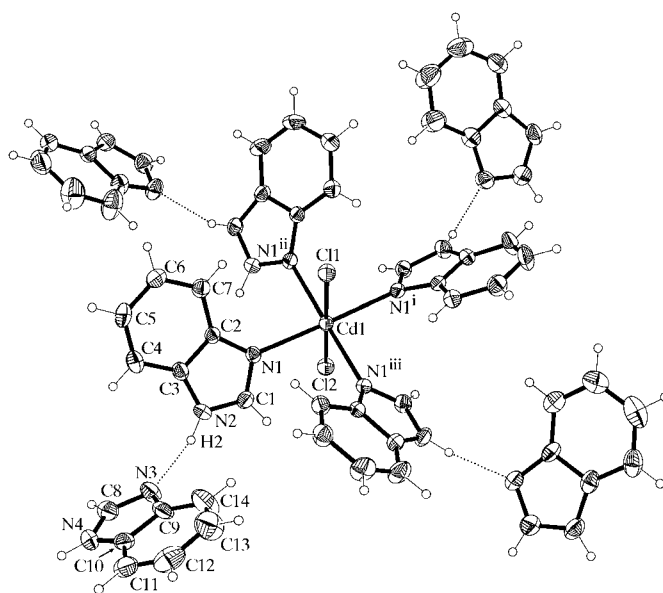


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii and dotted lines indicate hydrogen bonds. [Symmetry codes: (i) 1 - *x*, 1 - *y*, *z*; (ii) 1 - *y*, *x*, *z*; (iii) *y*, 1 - *x*, *z*.]

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, °).

*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.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...N3	0.86	2.07	2.836 (4)	149
N4—H4A...Cl1 ⁱⁱⁱ	0.86	2.62	3.377 (4)	147
C1—H1...Cg1 ^{iv}	0.93	2.87	3.675 (4)	146
C8—H8...Cg2 ^{iv}	0.93	2.61	3.525 (5)	167
C6—H6...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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. 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: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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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