Bis[2-(3-pyridinio)benzimidazolium] di-μ-chloro-bis[trichlorocadmium(II)]

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The title compound, $(C_{12}H_{11}N_3)_2[Cd_2Cl_8]$, consists of two discrete 2-(3-pyridinio)benzimidazolium cations and one $[Cd_2Cl_8]^{4-}$ anion. The dimeric $[Cd_2Cl_8]^{4-}$ anion lies about an inversion centre and consists of two distorted [CdCl$_5$] trigonal bipyramids which share a common edge. The two Cd atoms are each coordinated by two μ-Cl atoms and three terminal Cl atoms, with a Cd···Cd separation of 3.9853 (6) Å. The packing displays two-dimensional hydrogen-bonded sheets, which are further linked by C—H···Cl contacts and π–π stacking interactions to yield a three-dimensional network.

Comment

Crystal engineering of inorganic–organic hybrid materials is based on a modular approach, where discrete building blocks are connected into extended networks. In the search for reliable strategies for crystal synthesis by design, a key goal is the identification and exploitation of robust synthons to control the relative orientation of the molecular component of the solid. Among the usual interactions found to assemble the molecular crystal, hydrogen-bonding interactions have attracted the most attention. In the case of transition metal chloride complexes, the M—Cl moieties (M is a transition metal) can act as good hydrogen-bond acceptors (Gillon *et al.*, 2000; Lewis & Orpen, 1998; Luque *et al.*, 2002). We report here the title complex salt, (I), composed of a novel $[Cd_2Cl_8]^{4-}$ anion and two protonated 2-(3-pyridinio)benzimidazolium cations, in which N—H···Cl hydrogen bonds and π–π stacking interactions aggregate the anions and cations into a three-dimensional network.

(I)
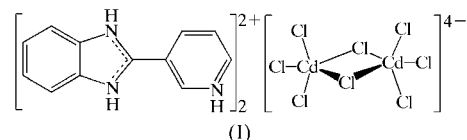
As shown in Fig. 1, compound (I) is composed of two 2-(3-pyridinio)benzimidazolium cations and a novel $[Cd_2Cl_8]^{4-}$ anion, which lies about an inversion centre, chosen for convenience to be $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In the unique cation, the pyridyl ring is rotated out of the benzimidazole ring plane with a dihedral angle of 12.9 (2)°. The dimeric $[Cd_2Cl_8]^{4-}$ anion can best be described as consisting of two distorted [CdCl$_5$] trigonal bipyramids which share a common edge. The bridging Cl1 atom is axial to one Cd atom and equatorial to the other. The Cd1—Cl1—Cd1^i—Cl1^i ring (see Table 1 for symmetry code) is strictly planar because of the inversion centre. In the [CdCl$_5$] moiety, atoms Cl1, Cl3 and Cl4 are equatorial, while Cl2 and Cl1^i are axial. Atom Cd1 and the three equatorial atoms are almost coplanar, with Cd1 being 0.1305 (8) Å from the Cl1/Cl3/Cl4 plane and displaced toward the axial atom Cl2. According to the different classes of Cd—Cl bond lengths, a logical sequence is apparent: Cd—Cl(axial,bridging) = 2.7498 (12) Å > Cd—Cl(axial,terminal) = 2.6573 (13) Å > Cd—Cl(equatorial,bridging) = 2.5483 (12) Å > Cd—Cl(equatorial,terminal) = 2.4605 (11) and 2.4325 (13) Å (Table 1). There is clearly no Cd—Cd bond in the dimer, the Cd···Cd
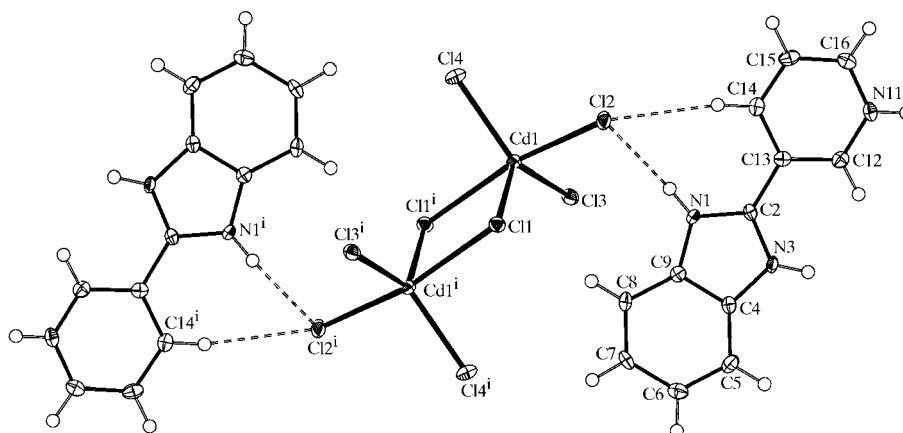

Figure 1
The structure of (I), showing the $[Cd_2Cl_8]^{4-}$ anion and the two inversion-related cations. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

distance of 3.9853 (6) Å being longer than the value of 3.53 Å found for the Cd···Cd distance in the dimeric $[Cd_2Cl_6]^{2-}$ anion (Bart *et al.*, 1980).

The dimeric $[Cd_2Cl_8]^{4-}$ anion of (I) exhibits a new coordination geometry, although it has been studied as part of a larger Cd–Ni compound (Chesnut *et al.*, 1999) which had terminal Cl atoms bonded to Ni atoms. Other dimeric Cd anions, such as $[Cd_2Cl_6]^{2-}$ (Bart *et al.*, 1980), have been described, but the Cd atoms have distorted tetrahedral geometry. In some polymeric structures (Charles *et al.*, 1984; Puget *et al.*, 1991; Doudin & Chapuis, 1992), the Cd centre generally displays octahedral coordination.

In the crystal lattice of (I), there are hydrogen-bonding and π–π stacking interactions. There are both N—H···Cl and C—H···Cl interactions between the 2-(3-pyridinio)benzimidazolium cations and the dimeric $[Cd_2Cl_8]^{4-}$ anions (Table 2). The N—H···Cl interactions generate a sheet structure, as shown in Fig. 2. In addition, there are π–π stacking interactions between adjacent aromatic and pyridine rings, as shown in Fig. 3. The centroid–centroid separation of rings N11/C12–C16 and C4–C9($x, \frac{1}{2} - y, z - \frac{1}{2}$) is 3.592 (6) Å, and the shortest interatomic separation is 3.345 (7) Å between atoms C14 and C8($x, \frac{1}{2} - y, z - \frac{1}{2}$). These interactions, together with C—H···Cl interactions involving atoms C12 and C16 (Table 2), generate a three-dimensional network.
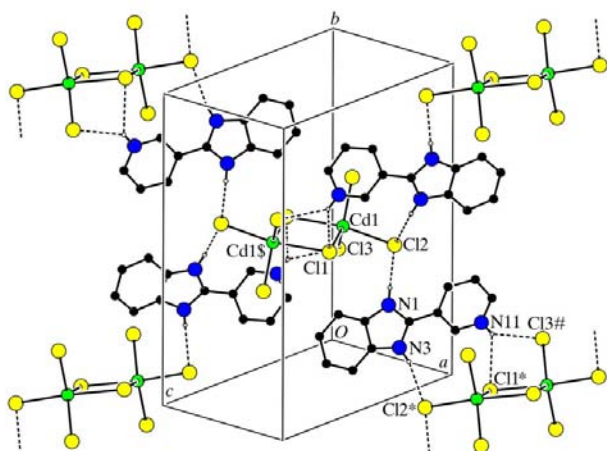

Figure 2
A view showing part of the hydrogen-bonded sheet in the crystal structure of (I). Atoms labelled with a dollar ($), asterisk (*) or hash (#) symbol are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(2 - x, y - \frac{1}{2}, \frac{1}{2} - z)$ and $(1 - x, \frac{1}{2} - y, z - \frac{1}{2})$, respectively.
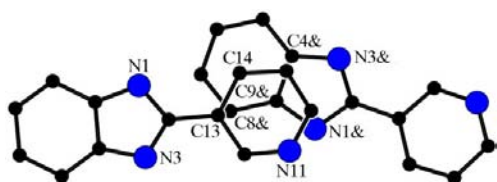

Figure 3
A view showing the π–π overlap of the two cations of (I). Atoms labelled with an ampersand (&) are at the symmetry position $(x, \frac{1}{2} - y, z - \frac{1}{2})$.

Experimental

2-(3-Pyridyl)benzimidazole was synthesized according to the literature method of Alcalde *et al.* (1992). An aqueous solution (20 ml) of 2-(3-pyridyl)benzimidazole (1.6 mmol), $CdCl_2$ (1.2 mmol) and HCl (0.2 ml) was stirred continuously for about 30 min. The solution was allowed to stand at room temperature for several days and produced colourless crystals of (I) (yield 81%). Analysis calculated for $C_{24}H_{22}Cd_2Cl_8N_6$: C 31.92, H 2.46, N 9.31%; found: C 32.12, H 2.71, N 9.37%. IR (KBr, ν, cm^{-1}): 3468 (*s*), 1625 (*s*), 1526 (*s*), 1378 (*s*), 1261 (*m*), 1114 (*m*), 876 (*s*), 811 (*s*), 765 (*m*), 666 (*m*), 527 (*m*), 488 (*m*).

Crystal data

$(C_{12}H_{11}N_3)_2[Cd_2Cl_8]$	$D_x = 2.029$ Mg m^{-3}
$M_r = 902.88$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3960
$a = 7.5295$ (5) Å	reflections
$b = 15.8570$ (13) Å	$\theta = 3.1–25.0°$
$c = 12.3755$ (9) Å	$\mu = 2.19$ mm^{-1}
$\beta = 90.457$ (6)°	$T = 293$ (2) K
$V = 1477.53$ (19) Å^3	Prism, colourless
$Z = 2$	$0.20 \times 0.15 \times 0.06$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	2593 independent reflections
ω scans	2209 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.058$
$T_{min} = 0.643$, $T_{max} = 0.880$	$\theta_{max} = 25.0°$
9164 measured reflections	$h = -8 \rightarrow 8$
	$k = -15 \rightarrow 18$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 2.7025P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.091$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.16$	$\Delta\rho_{max} = 0.74$ e Å^{-3}
2593 reflections	$\Delta\rho_{min} = -0.58$ e Å^{-3}
181 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cd1—Cl4	2.4325 (13)	Cd1—Cl2	2.6573 (13)
Cd1—Cl3	2.4605 (12)	Cd1—Cl1^i	2.7498 (12)
Cd1—Cl1	2.5483 (12)		
Cl4—Cd1—Cl3	127.27 (4)	Cl3—Cd1—Cl1	121.09 (4)
Cl4—Cd1—Cl1	110.80 (4)	Cl2—Cd1—Cl1^i	167.89 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl2	0.86	2.33	3.152 (4)	161
N3—H3···Cl2^{ii}	0.86	2.35	3.126 (4)	150
N11—H11···Cl1^{ii}	0.86	2.72	3.306 (4)	127
N11—H11···Cl3^{iii}	0.86	2.49	3.182 (4)	138
C12—H12···Cl1^{iv}	0.93	2.75	3.396 (5)	128
C14—H14···Cl2	0.93	2.71	3.623 (5)	168
C16—H16···Cl4^v	0.93	2.59	3.458 (5)	156

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

All H atoms were visible in difference maps and were treated as riding atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Version 1.70.01; Farrugia, 1999); molecular graphics: *SHELXL97* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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