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N,*N*′-Bis(3-pyridiniomethyl)-4,4′-benzidinediium tetrachloride dihydrate

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Key indicators

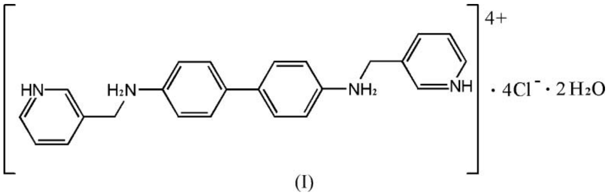
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.034
wR factor = 0.102
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{24}H_{26}N_4^{4+}\cdot 4Cl^-\cdot 2H_2O$, the cation possesses a crystallographically imposed centre of symmetry. The crystal structure is stabilized by intermolecular N—H⋯Cl, N—H⋯O and O—H⋯Cl hydrogen bonds, and by π–π stacking interactions.

Comment

Recently a number of research groups have focused on the investigation of the host–guest inclusion complexes (Kim, 2002; Harada, 2001; Ballardini *et al.*, 2001; Balzani *et al.*, 2000; Raymo & Stoddart, 1999; Pease *et al.*, 2001) involving a relatively new family of macrocyclic compounds, the cucurbit[*n*]urils (CB[*n*]) (Freeman *et al.*, 1981; Day & Arnold, 2000; Day *et al.*, 2002; Kim *et al.*, 2000). Among them, a series of rotaxanes, catenanes and other structures containing an 'axle' compound with different residues have been studied, which can develop strong intermolecular interactions with CB[*n*] (Kim *et al.*, 2004; Tuncel & Steinke, 1999; Jeon *et al.*, 1996; Meschke *et al.*, 1998; Lee *et al.*, 2001*a*,*b*). In this paper, we present the crystal structure of the new 'axle' polyaromatic title compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The *N*,*N*′-bis(3-pyridiniomethyl)-4,4′-benzidinediium cation possesses crystallographically imposed C_i symmetry, the inversion centre being located at the mid-point of the C11—C11*a* bond [symmetry code: (*a*) $1 - x, 2 - y, -z$]. The cation forms a step-like conformation with all four N atoms protonated. The dihedral angle between the pyridinium ring and the benzene ring is 8.20 (6)°. In the crystal structure, molecules are linked into one-dimensional chains running parallel to the [101] direction through a network of intermolecular hydrogen interactions (Table 1) involving the protonated amine N1 atom, the water molecule and the Cl1 anion. In this arrangement, weak π–π stacking interactions are observed between the pyridinium and benzene rings of adjacent chains [$Cg1\cdots Cg1^{vi}$ = 3.939 (3) Å; $Cg1\cdots Cg2^{vii}$ = 4.145 (3) Å; *Cg*1 and *Cg*2 are the centroids of the N1/C1–C6 pyridinium ring and the C13–C18 benzene ring, respectively; symmetry codes: (vi) $-x, 1 - y, 2 - z$; (vii) $1 - x, 1 - y, 1 - z$]. The chains are further linked *via* N—H⋯Cl and O—H⋯Cl hydrogen bonds (Table 1) to form supramolecular layers (Fig. 2).

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Experimental

A solution of 3-pyridinecarboxaldehyde (2.12 g 0.02 mol) in CH_3OH (50 ml) was added to a stirred solution of benzidine dihydrochloride (2.57 g, 0.01 mol) in CH_3OH (250 ml) on an oil bath at 333 K for 5 h. To the reaction mixture, $NaBH_4$ (0.95 g, 0.025 mol) was added in small amounts on an ice bath for 8 h. The insoluble residue was removed by filtration and the filtrate was neutralized with HCl to pH 6–7 and filtered again. Excess HCl solution (36%) was added to the final filtrate. The solvent was removed, and the residue was then dissolved in 300 ml of ethanol. Single crystals of (I) were obtained after several days on slow evaporation of the solvent.

Crystal data

$C_{24}H_{26}N_4^{4+}\cdot 4Cl^-\cdot 2H_2O$
$M_r = 548.32$
Triclinic, $P\overline{1}$
$a = 8.9764\ (17)$ Å
$b = 9.1437\ (18)$ Å
$c = 9.5321\ (18)$ Å
$\alpha = 63.838\ (3)°$
$\beta = 78.558\ (3)°$
$\gamma = 70.586\ (3)°$
$V = 661.1\ (2)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.48$ mm^{-1}
$T = 273\ (2)$ K
0.21 × 0.17 × 0.14 mm

Data collection

Bruker SMART APEX II CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.907$, $T_{\max} = 0.936$
6382 measured reflections
2395 independent reflections
2254 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.102$
$S = 1.08$
2395 reflections
162 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl1	0.90	2.16	3.0514 (15)	169
N1—H1A···O1$W^{\rm i}$	0.90	1.81	2.706 (2)	177
O1W—H1WA···Cl1$^{\rm ii}$	0.83 (3)	2.23 (3)	3.0476 (19)	169 (2)
N2—H2···Cl2$^{\rm iii}$	0.86	2.11	2.9701 (16)	174
O1W—H1WB···Cl2	0.82 (3)	2.31 (3)	3.0964 (18)	161 (3)

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

Water H atoms were located in a difference Fourier synthesis and refined freely. All other H atoms were placed in calculated positions and refined as riding, with C—H = 0.93–0.97 Å, N—H = 0.86–0.90 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

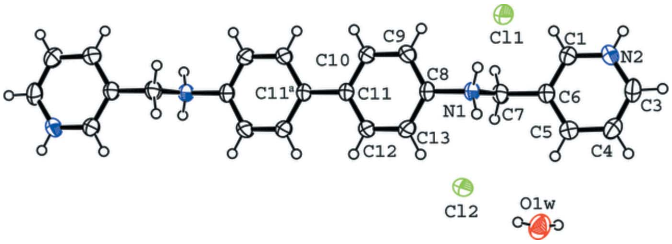

Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (*a*) $1-x, 2-y, -z$.]

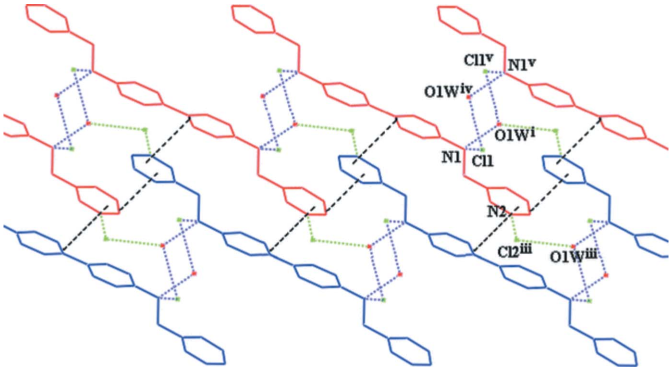

Figure 2
One dimensional supramolecular chain (in red or blue colour) and packing diagram of (I). Hydrogen bonds and π–π interactions are shown as dashed lines. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, 1-y, 1-z$; (iii) $x, y, z+1$; (iv) $x, y+1, z$; (v) $-x, 2-y, 1-z$.]

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