Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5,12-Dimethylpyrazino[1,2-*a*:4,5-*a*′]-dibenzimidazole-5,12-diium dichloride dihydrate

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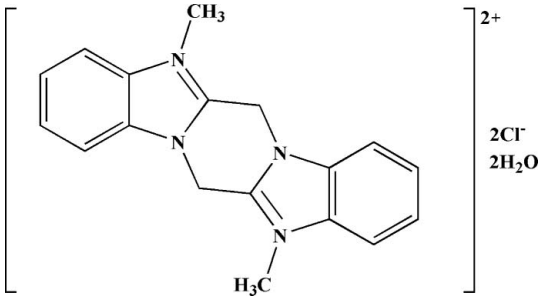
Received 25 September 2012; accepted 12 November 2012

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.114; data-to-parameter ratio = 13.2.

The title hydrated salt, $C_{18}H_{18}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$, sits about an inversion centre, such that the asymmetric unit contains one half-molecule. In the crystal, hydrogen bonds occur between the water molecules and chloride anions, and there is π–π stacking of the benzene and imidazole rings of inversion-related pairs of molecules, with a centroid–centroid distance of 3.704 (17) Å.

Related literature

For descriptions of clinical applications of the benzimidazole ring system, see: Harrell *et al.* (2004). For a related structure, see: Sun *et al.* (2010).



Experimental

Crystal data

$C_{18}H_{18}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$ M_r = 397.30
Monoclinic, $P2_1/c$
a = 8.1080 (12) Å
b = 9.0857 (14) Å
c = 12.9188 (19) Å
β = 94.426 (2)°
V = 948.8 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.36 mm^{-1}
T = 296 K
0.38 × 0.28 × 0.17 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.876, T_{max} = 0.943
4604 measured reflections
1681 independent reflections
1371 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.114
S = 1.07
1681 reflections
127 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1C···Cl1^{i}	0.83	2.33	3.1558 (19)	170
O1—H1D···Cl1^{ii}	0.83	2.37	3.190 (2)	170

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

Data collection: *APEX2* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The work was supported by 2009ZX09103–111, the China Postdoctoral Science Foundation (No. 2009041446), the Special Research Fund of the Education Department of Shaanxi Province (12 J K0631) and the Special Research Fund of Xianyang Normal University (11XSYK204). We thank the Instrumental Analysis Center of Northwest University for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2446).

References

Bruker (2002). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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supporting information

Acta Cryst. (2012). E**68**, o3398 [doi:10.1107/S1600536812046594]

5,12-Dimethylpyrazino[1,2-*a*:4,5-*a*′]dibenzimidazole-5,12-diium dichloride dihydrate

Jie Han, Ming-gao Zhao, Jun Zhang, Lan Ma and Guang Fan

S1. Comment

Bis-benzimidazoles are DNA-minor grove binding agents that possess anti-tumor activity. The benzimidazole ring system is present in clinically approved antihistamines, antivirals, anthelmintics, and antiulcer medications (Harrell *et al.*, 2004). In addition to their biological activity, there are numerous other studies, including coordination and corrosion inhibitor abilities of benzimidazoles. Bis-benzimidazoles are also strong chelating agents (Sun *et al.*, 2010). Some of these derivatives are used as photographic materials and dyes. As part of our ongoing investigation of benzimidazole derivatives, the title compound was synthesized and its crystal structure is reported herein.

S2. Experimental

N-methylbenzene-1,2-diamine (2.5 mol), 2-chloroacetic acid (3 mmol), polyphosphoric acid (10 ml) and silica gel (1 g) were mixed and introduced in an open Erlenmeyer flask. The reaction mixture was irradiated in a domestic microwave oven for 3 min. After cooling to room temperature, methanol was added (20 ml) and the reaction mixture filtered. The filtrate was evaporated to dryness and subjected to column chromatography (10% hexane/ethyl acetate) to give green needle-like crystals of the title compound.

S3. Refinement

All H atoms attached to C atoms were generated in idealized positions and constrained to ride on their parent atoms, with C—H = 0.96 Å (methyl) and 0.93 Å (aromatic) with U_{iso}(H) = 1.2U_{eq}(C, aromatic) and U_{iso}(H) = 1.5U_{eq}(C, methyl). H atoms of water molecules were located in a difference Fourier map and refined with 1,2 and 1,3 distance restraints of 0.85 (2) Å and 1.39 (2) Å.

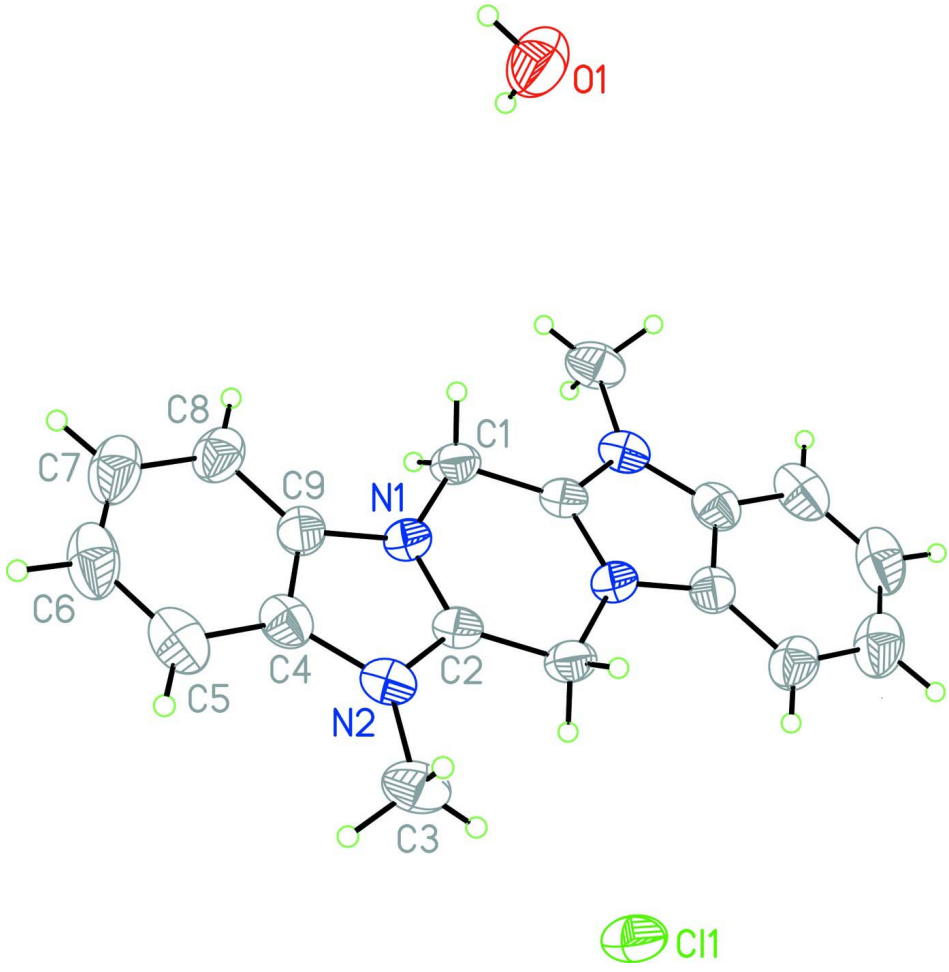

Figure 1

A view of the molecular structure of title compound. Displacement ellipsoids are drawn at the 35% probability level. Unlabelled atoms are related by inversion (1-x, -y, 1-z) to their labelled counterparts.

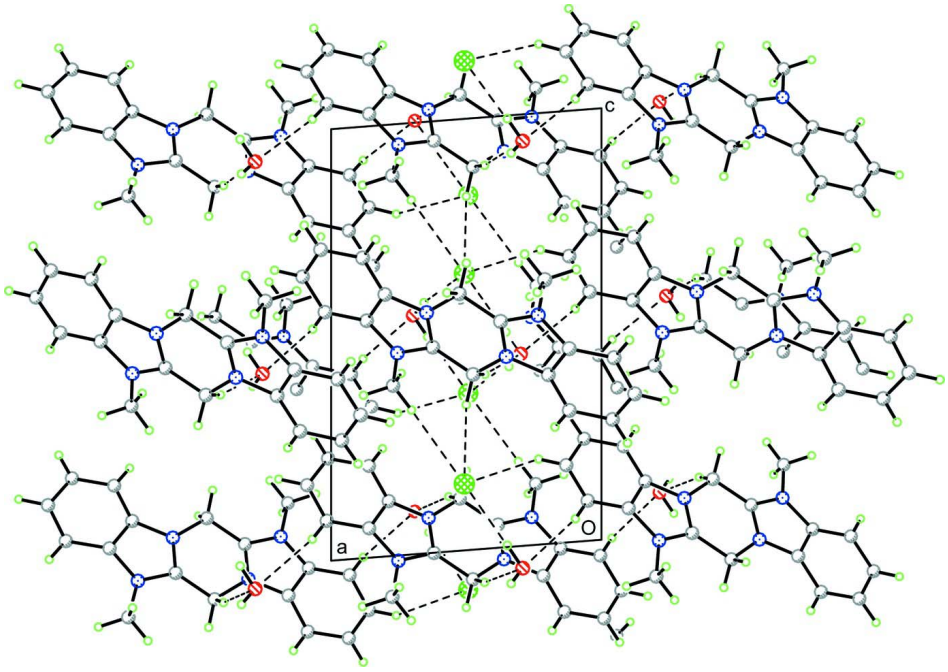

Figure 2

A three dimensional stacking diagram of (1) viewed down the *b* axis.

10,20-Dimethyl-3,10,13,20- tetraazapentacyclo[11.7.0.0^{3,11}.0^{4,9}.0^{14,19}]icosa- 1(20),4(9),5,7,10,14,16,18-octaene-10,20-diium

Crystal data

$C_{18}H_{18}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$
$M_r = 397.30$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.1080\ (12)$ Å
$b = 9.0857\ (14)$ Å
$c = 12.9188\ (19)$ Å
$\beta = 94.426\ (2)°$
$V = 948.8\ (2)$ Å^3
$Z = 2$
$F(000) = 416$
$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1814 reflections
$\theta = 2.5–26.8°$
$\mu = 0.36$ mm^{-1}
$T = 296$ K
Block, white
0.38 × 0.28 × 0.17 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.876$, $T_{max} = 0.943$
4604 measured reflections
1681 independent reflections
1371 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.5°$
$h = -9\rightarrow 9$
$k = -10\rightarrow 10$
$l = -10\rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.114$
$S = 1.07$
1681 reflections
127 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.1961P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.49232 (8)	0.17546 (7)	0.85285 (4)	0.0755 (3)
N1	0.35268 (18)	0.00311 (15)	0.44209 (10)	0.0454 (4)
N2	0.2397 (2)	0.17478 (16)	0.53127 (12)	0.0521 (4)
O1	0.7107 (3)	0.0906 (2)	0.05725 (17)	0.0961 (6)
C1	0.4743 (2)	−0.0970 (2)	0.40528 (14)	0.0532 (5)
H1A	0.5002	−0.0687	0.3360	0.064*
H1B	0.4301	−0.1962	0.4021	0.064*
C2	0.3745 (2)	0.09265 (19)	0.52381 (13)	0.0462 (4)
C3	0.2198 (3)	0.2890 (2)	0.60909 (19)	0.0701 (6)
H3A	0.2912	0.2682	0.6701	0.105*
H3B	0.1069	0.2908	0.6268	0.105*
H3C	0.2482	0.3830	0.5815	0.105*
C4	0.1255 (2)	0.1382 (2)	0.44954 (16)	0.0557 (5)
C5	−0.0348 (3)	0.1869 (3)	0.4213 (2)	0.0725 (7)
H5	−0.0854	0.2590	0.4590	0.087*
C6	−0.1142 (3)	0.1222 (3)	0.3345 (2)	0.0825 (8)
H6	−0.2216	0.1515	0.3136	0.099*
C7	−0.0399 (3)	0.0149 (3)	0.2772 (2)	0.0805 (7)
H7	−0.0981	−0.0247	0.2188	0.097*
C8	0.1178 (3)	−0.0338 (2)	0.30476 (16)	0.0642 (6)
H8	0.1682	−0.1056	0.2667	0.077*
C9	0.1975 (2)	0.0297 (2)	0.39233 (14)	0.0509 (5)
H1C	0.653 (3)	0.101 (3)	0.0016 (12)	0.081 (8)*
H1D	0.667 (4)	0.021 (2)	0.087 (2)	0.105 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0922 (5)	0.0875 (5)	0.0477 (3)	0.0113 (3)	0.0113 (3)	−0.0030 (2)
N1	0.0513 (9)	0.0469 (8)	0.0380 (8)	0.0018 (6)	0.0036 (6)	0.0004 (6)
N2	0.0584 (10)	0.0490 (9)	0.0508 (9)	0.0069 (7)	0.0152 (7)	0.0038 (6)
O1	0.0995 (15)	0.1007 (15)	0.0839 (14)	−0.0151 (12)	−0.0199 (11)	0.0121 (12)
C1	0.0599 (12)	0.0587 (11)	0.0414 (9)	0.0051 (9)	0.0068 (8)	−0.0074 (8)
C2	0.0525 (11)	0.0475 (10)	0.0396 (9)	0.0030 (8)	0.0103 (8)	0.0028 (7)
C3	0.0826 (15)	0.0569 (12)	0.0742 (14)	0.0093 (10)	0.0278 (12)	−0.0077 (10)
C4	0.0539 (11)	0.0548 (10)	0.0593 (12)	0.0024 (9)	0.0102 (9)	0.0165 (9)
C5	0.0604 (13)	0.0688 (14)	0.0901 (17)	0.0111 (10)	0.0171 (12)	0.0306 (12)
C6	0.0567 (14)	0.0892 (17)	0.0993 (19)	−0.0038 (12)	−0.0093 (13)	0.0444 (16)
C7	0.0726 (16)	0.0880 (17)	0.0773 (16)	−0.0122 (13)	−0.0181 (13)	0.0283 (14)
C8	0.0688 (13)	0.0683 (13)	0.0538 (12)	−0.0082 (10)	−0.0063 (10)	0.0120 (10)
C9	0.0504 (11)	0.0549 (10)	0.0472 (10)	−0.0026 (8)	0.0023 (8)	0.0117 (8)

Geometric parameters (Å, º)

N1—C2	1.334 (2)	C3—H3B	0.9600
N1—C9	1.389 (2)	C3—H3C	0.9600
N1—C1	1.448 (2)	C4—C9	1.388 (3)
N2—C2	1.333 (2)	C4—C5	1.394 (3)
N2—C4	1.390 (3)	C5—C6	1.382 (4)
N2—C3	1.462 (3)	C5—H5	0.9300
O1—H1C	0.830 (10)	C6—C7	1.389 (4)
O1—H1D	0.827 (10)	C6—H6	0.9300
C1—C2^{i}	1.473 (3)	C7—C8	1.374 (3)
C1—H1A	0.9700	C7—H7	0.9300
C1—H1B	0.9700	C8—C9	1.385 (3)
C2—C1^{i}	1.473 (3)	C8—H8	0.9300
C3—H3A	0.9600		
C2—N1—C9	108.69 (15)	H3A—C3—H3C	109.5
C2—N1—C1	126.20 (15)	H3B—C3—H3C	109.5
C9—N1—C1	124.93 (15)	C9—C4—N2	106.96 (16)
C2—N2—C4	108.25 (15)	C9—C4—C5	120.5 (2)
C2—N2—C3	125.56 (18)	N2—C4—C5	132.5 (2)
C4—N2—C3	126.12 (17)	C6—C5—C4	116.4 (2)
H1C—O1—H1D	104 (3)	C6—C5—H5	121.8
N1—C1—C2^{i}	109.51 (14)	C4—C5—H5	121.8
N1—C1—H1A	109.8	C5—C6—C7	122.5 (2)
C2^{i}—C1—H1A	109.8	C5—C6—H6	118.7
N1—C1—H1B	109.8	C7—C6—H6	118.7
C2^{i}—C1—H1B	109.8	C8—C7—C6	121.4 (2)
H1A—C1—H1B	108.2	C8—C7—H7	119.3
N2—C2—N1	109.82 (16)	C6—C7—H7	119.3
N2—C2—C1^{i}	125.99 (16)	C7—C8—C9	116.3 (2)

N1—C2—C1^{i}	124.19 (15)	C7—C8—H8	121.8
N2—C3—H3A	109.5	C9—C8—H8	121.8
N2—C3—H3B	109.5	C8—C9—C4	122.85 (19)
H3A—C3—H3B	109.5	C8—C9—N1	130.88 (19)
N2—C3—H3C	109.5	C4—C9—N1	106.27 (16)
C2—N1—C1—C2^{i}	3.6 (3)	N2—C4—C5—C6	−178.57 (19)
C9—N1—C1—C2^{i}	178.11 (15)	C4—C5—C6—C7	−0.4 (3)
C4—N2—C2—N1	−0.86 (19)	C5—C6—C7—C8	0.6 (4)
C3—N2—C2—N1	−177.88 (17)	C6—C7—C8—C9	0.0 (3)
C4—N2—C2—C1^{i}	179.73 (17)	C7—C8—C9—C4	−0.8 (3)
C3—N2—C2—C1^{i}	2.7 (3)	C7—C8—C9—N1	178.01 (18)
C9—N1—C2—N2	1.22 (19)	N2—C4—C9—C8	179.65 (17)
C1—N1—C2—N2	176.48 (16)	C5—C4—C9—C8	1.1 (3)
C9—N1—C2—C1^{i}	−179.35 (16)	N2—C4—C9—N1	0.56 (19)
C1—N1—C2—C1^{i}	−4.1 (3)	C5—C4—C9—N1	−177.98 (17)
C2—N2—C4—C9	0.16 (19)	C2—N1—C9—C8	179.92 (19)
C3—N2—C4—C9	177.16 (17)	C1—N1—C9—C8	4.6 (3)
C2—N2—C4—C5	178.5 (2)	C2—N1—C9—C4	−1.08 (19)
C3—N2—C4—C5	−4.5 (3)	C1—N1—C9—C4	−176.42 (16)
C9—C4—C5—C6	−0.5 (3)		

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*C*···Cl1^{ii}	0.83	2.33	3.1558 (19)	170
O1—H1*D*···Cl1^{i}	0.83	2.37	3.190 (2)	170

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