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N,*N*′-Bis(benzimidazol-1-ium-2-ylmethyl)-*N*,*N*′-bis(benzimidazol-2-ylmethyl)cyclohexane-1,2-*trans*-diamine bis(perchlorate) dihydrate

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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.004 Å
R factor = 0.059
wR factor = 0.174
Data-to-parameter ratio = 12.2

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

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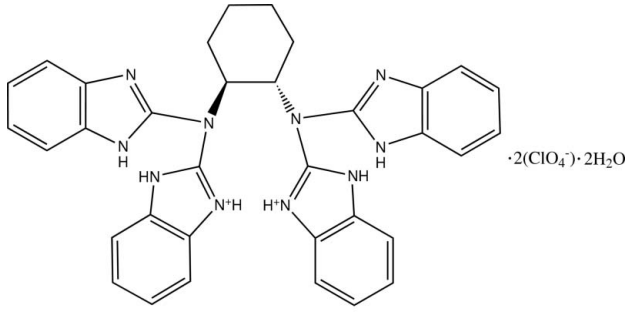
In the cation of the title compound, $C_{38}H_{40}N_{10}^{2+}\cdot 2ClO_4^-\cdot 2H_2O$, the cyclohexanediamine group has a twofold axis and two of the four pendant benzimidazole groups are protonated. There are hydrogen bonds and π–π interactions in the crystal structure.

Comment

Histidine is an important ligand in iron, copper, zinc and manganese metalloproteins, such as superoxide dismutases, lipoxygenase, tyrosinase, amine oxidase and hemocyanin (Que & Raymond, 1996; Kaim & Rall, 1996). *N*,*N*,*N*′,*N*′-Tetrakis(2-benzimidazolymethyl)-1,2-*trans*-diaminocyclohexane (ctb) is a benzimidazole-rich ligand, which has the advantage that the basicity of the coordinating group approximates that of histidine (pK_b: histidine = 7.96 and benzimidazole = 8.47; Main, 1992). We obtained the title compound, (I), $H_2ctb^{2+}\cdot 2ClO_4^-\cdot 2H_2O$, in the process of synthesizing a ctb–metal complex in 95% ethanol.



(I)

In (I), the H_2ctb^{2+} cation has a twofold axis (Fig. 1). All four benzimidazolyl groups lie on one side of the cyclohexane ring, which is in a chair form similar to the ring in 1,2-cyclohexanediaminetetraacetic acid. The amine N atoms [N1 and N1^{i}; symmetry code: (i) $-x, y, \frac{1}{2}-z$] adopt a *trans* conformation. There are intramolecular N—H···N hydrogen bonds (N5—H5···N2^{i} and the symmetry-related bond), and also N—H···O and O—H···O intermolecular hydrogen bonds (Table 1) between H_2ctb^{2+} and H_2O or perchlorate, producing a three-dimensional framework (Fig. 2).

In the H_2ctb^{2+} cation, two five-membered rings, denoted *A* (atoms N2/C5/N3/C6/C11) and *B* (N4/C13/N5/C19/C14), are stacked 3.471 (2) Å apart, the dihedral angle between them being 18.88 (2)°. Furthermore, intermolecular π–π interactions exist between ring *A* and ring B at $(x, 1-y, z-\frac{1}{2})$, the distance between the centroids of the rings being 3.710 (2) Å and the dihedral angle 9.58 (2)° (Fig. 3).

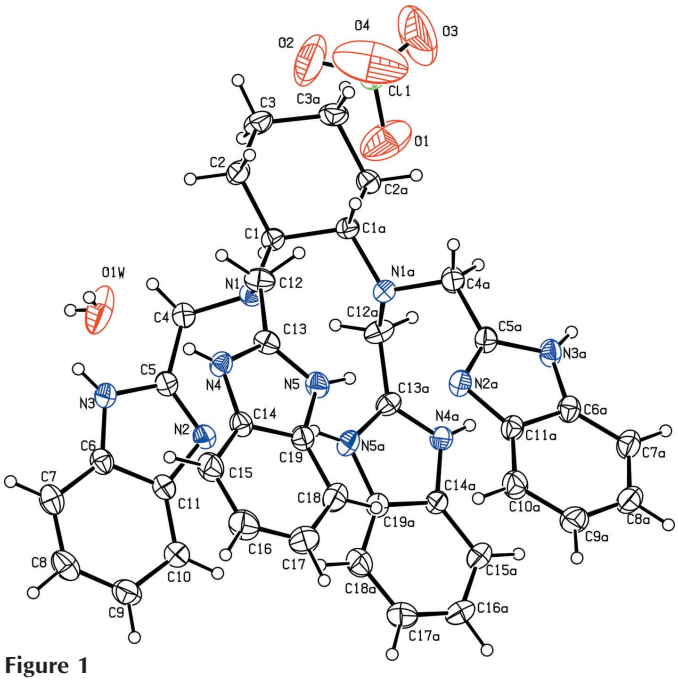


Figure 1
The structure of (I), showing displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (*a*) $-x, y, \frac{1}{2}-z$.]

Experimental

All reagents and solvents were used as obtained without further purification. Compound (I) was synthesized by refluxing stoichiometric quantities (1:2 molar ratio) of ctb (0.32 g, 0.5 mmol) and ferric perchlorate (0.52 g, 1 mmol) in 95% ethanol (30 ml) at 333 K for 6 h. The solution was cooled to room temperature, filtered and evaporated to obtain the product (yield 42%). Crystals of (I) were grown from an ethanol solution by slow evaporation.

Crystal data

$C_{38}H_{40}N_{10}^{2+}\cdot 2ClO_4^-\cdot 2H_2O$
M_r = 871.73
Orthorhombic, *Pbcn*
a = 16.4609 (10) Å
b = 17.6108 (11) Å
c = 13.8677 (9) Å
V = 4020.1 (4) Å^3
Z = 4
D_x = 1.440 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5855 reflections
θ = 2.2–24.8°
μ = 0.23 mm^{-1}
T = 292 (2) K
Block, pink
0.40 × 0.30 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
19135 measured reflections
3536 independent reflections
2954 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°
$h = -19 \rightarrow 14$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.174
S = 1.04
3536 reflections
291 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 3.4612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

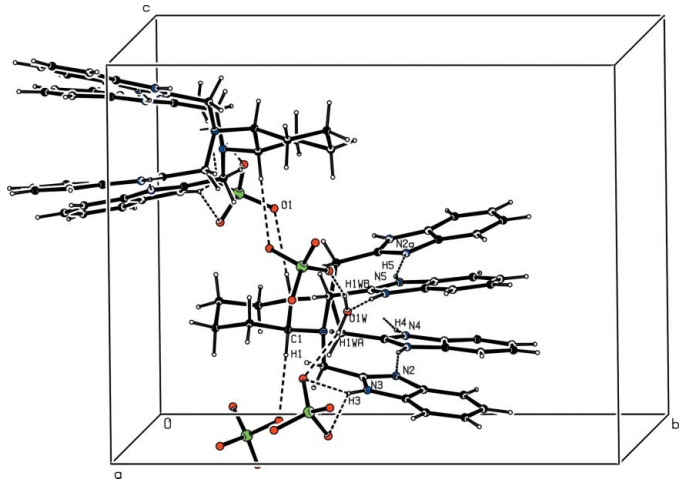


Figure 2
The linking of the molecules *via* hydrogen bonds (dashed lines).

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···N2^{i}	0.85 (1)	2.24 (2)	3.053 (3)	160 (3)
N3—H3···O2^{ii}	0.85 (1)	2.38 (2)	3.081 (5)	140 (2)
N3—H3···O4^{ii}	0.85 (1)	2.54 (2)	3.342 (8)	158 (3)
N4—H4···O1*W*	0.85 (1)	1.90 (1)	2.744 (3)	172 (3)
O1*W*—H1*WA*···O4^{ii}	0.81 (1)	2.02 (2)	2.808 (5)	162 (6)
O1*W*—H1*WB*···O3^{iii}	0.82 (1)	2.12 (2)	2.904 (5)	161 (3)
C1—H1···O1^{i}	0.98	2.47	3.446 (4)	175

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

H atoms bonded to C atoms were placed at calculated positions, with C—H distances of 0.93–0.97 Å, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). H atoms bonded to N atoms and the water O atom were located in difference density maps and refined with the restraints N—H = 0.86 (1) Å, O—H = 0.82 (1) Å and H1*WA*···H1*WB* = 1.34 (1) Å, but their U_{iso}(H) parameters were refined freely.

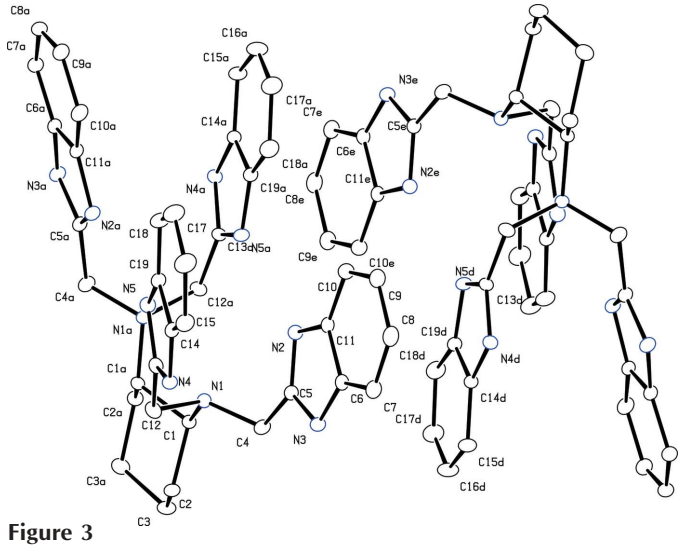


Figure 3
A view of the π–π stacking in the crystal structure. H atoms have been omitted. [Symmetry codes: (*a*) $-x, y, \frac{1}{2}-z$; (*d*) $x, 1-y, z-\frac{1}{2}$; (*e*) $-x, y, -\frac{1}{2}-z$.]

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* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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