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2,2′-{2,11-Bis[(3*H*-1,3-benzimidazol-1-ium-2-yl)-methyl]-5,8-dioxa-2,11-diazadodecane-1,12-diyl}-bis(3*H*-1,3-benzimidazol-1-ium) dichloride diperchlorate methanol disolvate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.088
wR factor = 0.267
Data-to-parameter ratio = 14.7

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

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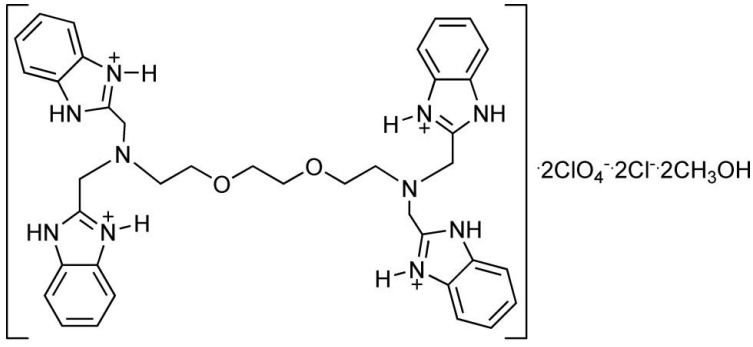
The title compound, $C_{38}H_{44}N_{10}O_2^{4+}\cdot 2ClO_4^-\cdot 2Cl^-\cdot 2CH_3OH$, crystallizes with the main molecule situated on a center of inversion. The ions are connected by intermolecular O—H···O, N—H···O and N—H···Cl hydrogen bonds.

Comment

Recently, multinuclear metal complexes containing multibenzimidazole ligands have attracted much attention for the development of superoxide dismutase (SOD) enzyme and nuclease mimics (Liao *et al.*, 2001; Liu *et al.*, 2004). Many metal complexes containing benzimidazole have been synthesized and characterized (Li *et al.*, 2003; Yang *et al.*, 2003; Yan *et al.*, 2004). The SOD-like activity of an *N*,*N*,*N*′,*N*′-tetrakis(2-benzimidazolylmethyl-1,4-diethyleneamino)glycol ether (EGTB) metal complex (Zhu *et al.*, 2002) attracted our interest. In the process of synthesizing EGTB metal complexes, we obtained the title compound, (I). Although methanoic acid was added as a bridging agent, it did not coordinate with the metal. In the acid conditions, the ligand EGTB is protonated, and the N atom in the benzimidazole ring has a positive charge. The counter-ions (chloride and perchlorate) and protons balance the charges.



(I)

The main geometric parameters of (I) are listed in Table 1 and the structure is illustrated in Fig. 1. Compound (I) has a crystallographically imposed inversion center. The distances of amino N to C atoms range from 1.450 (6) to 1.471 (6) Å, and the C—N bond lengths of benzimidazole from 1.303 (5) to 1.406 (6) Å. These bond lengths are similar to the distances in EDTB reported previously in our work (Qin *et al.*, 2004; Yan *et al.*, 2004). The four benzimidazole rings in (I) are each planar. The dihedral angle between the two independent benzimidazole least-squares planes is 10.05 (19)°.

The crystal packing of (I) (Fig. 2) features O—H···O, N—H···O and N—H···Cl hydrogen bonds (Table 2), which form between benzimidazole N atoms and O atoms from the

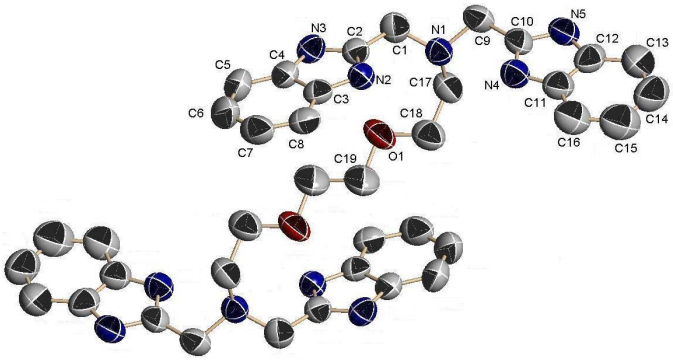


Figure 1
A view of the cation in (I), shown with 50% probability displacement ellipsoids. Unlabeled atoms are related to symmetry-equivalent labeled atoms by the symmetry code $(2-x, 2-y, 2-z)$. H atoms have been omitted for clarity

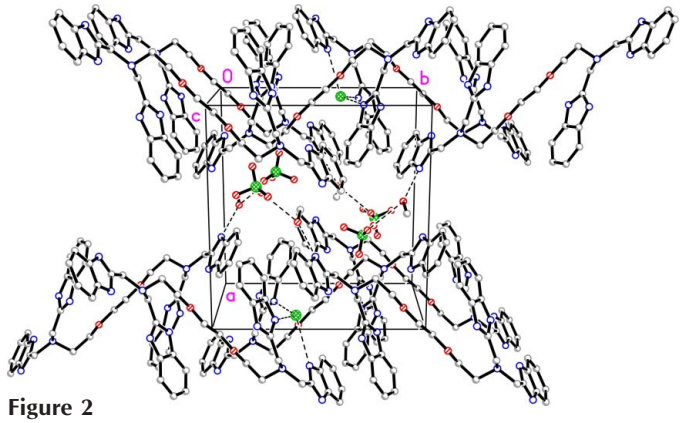


Figure 2
A packing diagram for (I), viewed approximately along the *c* axis, H atoms have been omitted for clarity. Dashed lines indicate hydrogen bonds.

methanol, benzimidazole N atom and chlorine anions, and O atoms from methanol and perchloride anions, respectively.

Experimental

The chemicals used for the synthesis were of reagent grade quality and used without further purification. EGTB was prepared as described before (Qin *et al.*, 2004). $Gd(ClO_4)_3$ (homemade, 0.125 mmol) was dissolved in methanol (20 ml) with methanoic acid (2 ml) and stirred at about 323 K. To this solution was added, dropwise, EGTB (0.25 mmol) dissolved in hot ethanol (20 ml) over a period of 15 min; the mixed solution was then stirred and refluxed for 30 min. The solution was filtered and the filtrate kept at room temperature. Light-yellow crystals were obtained from the filtrate after two weeks by slow evaporation of the solvent. Unfortunately, the crystals were of the ligand rather than the metal complex.

Crystal data

$C_{38}H_{44}N_{10}O_2^{4+}\cdot 2ClO_4^-\cdot 2Cl^-\cdot 2CH_4O$
$M_r = 1006.72$
Monoclinic, $P2_1/c$
$a = 14.043$ (2) Å
$b = 12.4625$ (17) Å
$c = 15.147$ (2) Å
$\beta = 107.328$ (2)°
$V = 2530.6$ (6) Å^3
$Z = 2$
$D_x = 1.321$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3280 reflections
$\theta = 2.4$–21.3°
$\mu = 0.30$ mm^{-1}
$T = 298$ (2) K
Block, light yellow
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.943$, $T_{max} = 0.971$
12 329 measured reflections
4399 independent reflections
2298 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.267$
$S = 0.96$
4399 reflections
300 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1829P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.450 (6)	C9—N1	1.470 (5)
C1—C2	1.477 (6)	C10—N5	1.303 (5)
C2—N3	1.322 (5)	C10—N4	1.327 (5)
C2—N2	1.325 (5)	C11—N4	1.372 (6)
C3—N2	1.364 (5)	C12—N5	1.406 (6)
C3—C4	1.393 (6)	C17—N1	1.471 (6)
C4—N3	1.379 (5)	C18—O1	1.412 (6)
N1—C1—C2	112.8 (4)	N1—C9—C10	109.9 (3)
N3—C2—N2	108.1 (4)	N5—C10—N4	109.0 (4)
N3—C2—C1	126.1 (4)	N5—C10—C9	127.0 (4)
N2—C2—C1	125.7 (4)	N4—C10—C9	124.0 (4)
N2—C3—C4	106.6 (4)	C12—C11—N4	106.5 (4)
N3—C4—C3	105.2 (4)	C11—C12—N5	105.9 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···Cl1^{i}	0.86	2.32	3.128 (4)	157
N3—H3···Cl1^{ii}	0.86	2.28	3.111 (4)	162
N4—H4···Cl1^{i}	0.86	2.30	3.106 (4)	156
N5—H5A···O2	0.86	1.83	2.649 (7)	159
O2—H2···O3^{iii}	0.82	2.42	2.815 (8)	111

Symmetry codes: (i) $1+x, y, 1+z$; (ii) $1+x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $1-x, 1-y, 1-z$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O—H, N—H and C—H distances of 0.82, 0.86, and 0.93–0.97 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}$(C,N) or $1.5U_{eq}$[C(methanol),O].

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: *SHELXL/PC* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL/PC*.

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