Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2-[6-(1*H*-Benzimidazol-2-yl)-2-pyridyl]-1*H*-benzimidazol-3-ium perchlorate monohydrate

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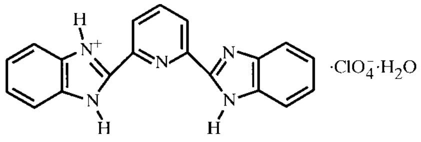
Received 10 December 1999
Accepted 21 March 2000

The title compound, $C_{19}H_{14}N_5^+\cdot ClO_4^-\cdot H_2O$, contains planar $C_{19}H_{14}N_5^+$ cations, perchlorate anions and water molecules. The two closest parallel cations (plane-to-plane distance of 3.41 Å), together with two neighbouring perchlorate anions and two water molecules, form an electrically neutral quasi-dimeric unit. Two acidic H atoms of the cation, both H atoms of the water molecule, the N atoms of the imidazole rings and three of the four O atoms of the perchlorate anion are involved in the hydrogen-bonding network within the dimeric unit. The remaining third acidic H atom of the imidazole rings and the water molecules complete a two-dimensional network of hydrogen bonds, thus forming puckered layers of dimers. The angle between the planes of two neighbouring dimeric units in the same layer is 33.25 (3)°.

Comment

Complexes of 2,6-bis(benzimidazol-2-yl)pyridine and its derivatives have been studied for more than 30 years because of their unusual coordination properties (Rüttimanm *et al.*, 1992) and unusual magnetic properties (Gütlich, 1981; Boča *et al.*, 1998). However, the structures of the free ligands have been reported only occasionally. We are aware of only one such example, the structure of 2-(1-methyl-3-benzimidazolinium-2-yl)-6-(1-methylbenzimidazol-2-yl)pyridine perchlorate, (II) (Petoud *et al.*, 1997). Here, we present the structure of the title compound, a similar free ligand, as its perchlorate monohydrate, (I).

A view of (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. All C and N atoms of the cation lie on one almost perfect plane. The mean deviation from this plane is 0.052 Å and the greatest deviation is 0.108 (2) Å for C4. In contrast, the corresponding cation in compound (II) is quite bent, with the planes of the benzimidazole units forming angles of about 30.5 and 45.3° with that of the central pyridine ring because of steric interactions between the opposing methyl groups that are in a *cis-cis* position with respect to the pyridine N atom. The positions of N3 and N5 in (I) are *trans-trans* with respect to N1. A similar conformation was observed in (II). In all metal complexes this position changes to *cis-cis*.



(I)

The aromatic C—C and C—N distances from both the benzimidazole and pyridine rings are within the usual range and this confirms the aromatic character of the pyridine and benzimidazole moieties. The protonation of atom N5 has no influence on the aromatic character of the benzimidazole moiety.

The structure of (I) contains cations stacked along the *a* axis. The neighbouring cations from adjacent stacks form a puckered layer in which the angle between the planes of adjacent cations is 33.25 (3)°. Pairs of puckered layers are held together by a system of hydrogen bonds involving the H atoms of the water molecules, the N atoms of the benzimidazole moieties and the O atoms of the perchlorate anions, and by van der Waals interactions. The hydrogen-bonding system (Table 2) thus connects together two stacked cations to form a quasi-dimeric unit with a plane-to-plane distance of 3.41 Å. Additional hydrogen bonds involving the water molecules and H14 of the benzimidazole moieties connect the quasi-dimers end on, to form the extended stacked puckered layers. Adjacent bilayers of dimers are held together by van der Waals interactions. It is very interesting that the interplanar distance between neighbouring cations that do not interconnect *via* hydrogen bonds is very similar (3.4 Å) to that for the cations that are linked by the hydrogen-bonding system.

The π-stacking found in (II) was not observed for (I); thus, an interaction of the π orbitals of two cations is not facilitated. The proton originating from the perchloric acid is localized on atom N5 and interacts with the O atom from the water molecule, thus forming interdimer hydrogen bonds. In compound (II), the acid H atoms are involved in hydrogen bonds

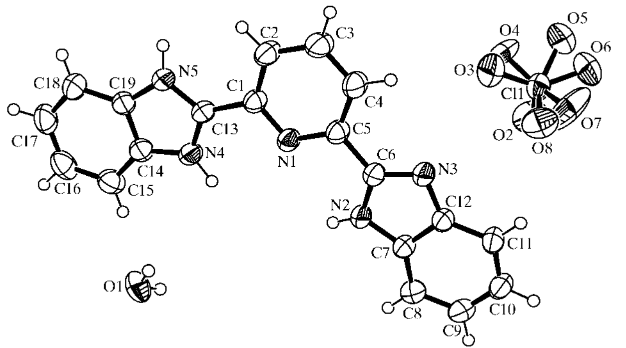


Figure 1
The structure and atom-numbering scheme of (I), showing 50% probability displacement ellipsoids. H atoms are shown as circles of an arbitrary radius.

between the unprotonated benzimidazole unit of one cation and the protonated unit of an adjacent cation, and *vice versa*, thus forming a quasi-dimeric unit (Petoud *et al.*, 1997). The hydrogen-bonding network in (I) is shown in Fig. 2.

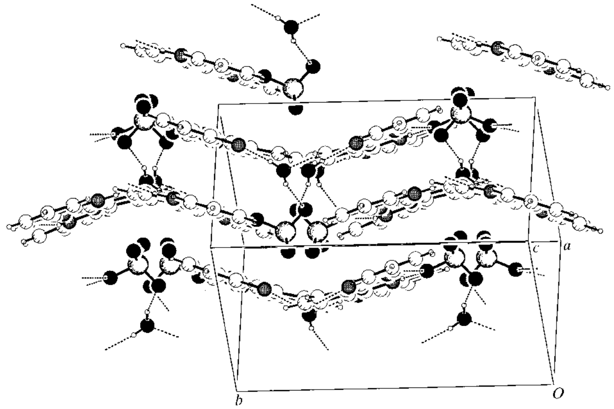


Figure 2
A packing diagram illustrating the hydrogen-bonding network in (I) and the system of puckered layers.

Experimental

Single crystals of (I) suitable for X-ray analysis were obtained from a mixture of $Fe(ClO_4)_3 \cdot 10H_2O$ (0.267 g, 0.5 mmol) in ethanol (10 ml) and 2,6-bis(benzimidazol-2-yl)pyridine (0.311 g, 1 mmol) in ethanol (20 ml) after two weeks at room temperature. This was actually an attempt to obtain an iron(III) perchlorate complex of the ligand. Single crystals denature above 353 K due to the loss of water, but they do not melt until 533 K.

Crystal data

$C_{19}H_{14}N_5^+ \cdot ClO_4^- \cdot H_2O$
$M_r = 429.82$
Monoclinic, $P2_1/n$
$a = 9.168$ (2) Å
$b = 15.111$ (3) Å
$c = 13.962$ (3) Å
$\beta = 101.98$ (2)°
$V = 1892.1$ (7) Å^3
$Z = 4$
$D_x = 1.509$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.98–11.59°$
$\mu = 0.247$ mm^{-1}
$T = 304$ (2) K
Needle, colourless
0.75 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.837$, $T_{\max} = 0.952$
4491 measured reflections
3716 independent reflections
2847 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 25.98°$
$h = -11 \rightarrow 2$
$k = -18 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 9.8%

Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.125$
$S = 1.023$
3716 reflections
322 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 0.5099P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0026 (11)

The positions of the amine and water H atoms were refined freely, together with their individual isotropic displacement parameters. All other H atoms were included in the refinement at geometrically calculated positions and refined using a riding model, with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the parent C atom. The perchlorate anion is disordered about an axis passing through Cl1 and O2. Two sets of positions were defined for the remaining three O atoms of the perchlorate anion and the site-occupancy factors of the two sets were refined while constraining their sum to 1.0.

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.335 (2)	N4—C13	1.331 (3)
N1—C1	1.341 (2)	N4—C14	1.382 (2)
N2—C6	1.345 (3)	C13—C1	1.466 (3)
N2—C7	1.378 (2)	C6—N3	1.323 (2)
N5—C13	1.329 (2)	C6—C5	1.467 (3)
N5—C19	1.383 (3)	N3—C12	1.384 (2)
C5—N1—C1	116.59 (16)	C13—N4—C14	109.00 (16)
C6—N2—C7	107.61 (16)	C6—N3—C12	104.59 (16)
C13—N5—C19	108.59 (17)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H4···O5$^{\rm i}$	0.82 (3)	2.23 (3)	3.048 (6)	170 (2)
N2—H4···O4$^{\rm i}$	0.82 (3)	2.22 (3)	2.910 (7)	138 (2)
N4—H9···O6$^{\rm i}$	0.92 (3)	2.03 (3)	2.830 (2)	144 (2)
N4—H9···O5$^{\rm i}$	0.92 (3)	2.04 (3)	2.959 (5)	176 (2)
N5—H14···O1$^{\rm ii}$	0.94 (4)	1.74 (4)	2.672 (3)	171 (3)
O1—H15···O2$^{\rm i}$	0.76 (4)	2.37 (4)	3.071 (3)	154 (3)
O1—H15···O6$^{\rm i}$	0.76 (4)	2.38 (4)	3.052 (7)	148 (3)
O1—H16···N3$^{\rm iii}$	0.80 (4)	2.02 (4)	2.806 (2)	169 (3)

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

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1993); data reduction: *REDU*4 (Stoe & Cie, 1988); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1998); software used to prepare material for publication: *SHELXL*97.

We acknowledge the support of the bilateral Slovak–Germany program (project SLA-005-97), the Slovak Grant Agency (project 1/6083/99), the Fonds der Chemischen Industrie and the Austrian Federal Ministry of Science and Transport (project No. GZ 70.023/2-Pr/4/97).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1095). Services for accessing these data are described at the back of the journal.

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