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Three-dimensional hydrogen-bonding supramolecular architecture of 2-(3-pyridinio)-5-(3-pyridyl)-1,3,4-oxadiazole perchlorate

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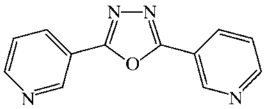
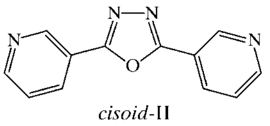
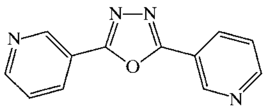
In the crystal structure of the title compound, $C_{12}H_9N_4O^+\cdot ClO_4^-$, the protonated cation adopts a *cis*-I conformation and approximately planar geometry. Each perchlorate anion acts as the acceptor of three C—H···O weak interactions, which, together with N—H···N and C—H···N hydrogen bonds between the protonated cations, extend this structure into a three-dimensional hydrogen-bonded network.

Comment

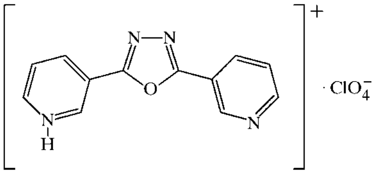
Bifunctional bridging ligands, for instance, 4,4′-bipyridine, have been used to construct a wide range of zero-, one-, two- or three-dimensional coordination supramolecules or polymers with interesting structural topologies and properties (Fujita, 1998; Hagrman *et al.*, 1999; Leininger *et al.*, 2000). However, compared with the well investigated linear 4,4′-N-donor bridging ligands, studies of 3,3′-N-donor species are still quite limited (Withersby *et al.*, 1999). Compounds of this type, at least theoretically, have a potential tendency to generate three typical isomers (two *cisoid* and one *transoid*, see scheme above) under appropriate conditions, which behavior is quite different from that of their 4,4′-N-donor analogs (Du & Zhao, 2003).


cisoid-I


cisoid-II


transoid

Recently, we have initiated a synthesis program for the construction of various coordination polymers or supramolecules with interesting extended frameworks based on the angular dipyridyl ligands 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo; Du *et al.*, 2003) and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (4-bpo; Du, Bu *et al.*, 2002; Du, Chen *et al.*, 2002). The specific geometry of this type of ligand may result in either discrete (*e.g.* molecular box) or divergent coordination networks (*e.g.* one-dimensional zigzag chain, two-dimensional grid sheet or three-dimensional interpenetrating diamondoid framework) upon metal complexation under appropriate conditions. In addition, it is well known that aromatic compounds of this type also exhibit interesting proton-sponge properties (Staab & Saupe, 1988; Robertson *et al.*, 1998), *i.e.* they can act as external proton acceptors through the formation of N—H···*Y* hydrogen bonds. Moreover, heteroatoms such as N and O with free electron pairs on the five-membered 1,3,4-oxadiazole ring could be considered as the potential active hydrogen-bonding acceptors needed to form an extended supramolecular network *via* hydrogen-bonding interactions. Taking into account all the above-mentioned aspects, the present work reports the crystal structure of the title compound, (I).


(I)

The crystal structure of (I) consists of a monoprotonated cation of 3-bpo, $C_{12}H_9N_4O^+$, as shown in Fig. 1, and a ClO_4^- counter-anion. All non-H atoms of the cation are nearly coplanar, the mean deviation of any atom from the best-fit plane being 0.061 (4) Å. The pyridinio and pyridyl rings make dihedral angles of 3.5 (3) and 4.5 (4)° with the central oxadiazole system, and the dihedral angle of the pyridinio and pyridyl rings is 8.0 (4)°. The mean and maximum deviations of any atoms from the best-fit plane of the pyridinio, pyridyl and oxadiazole rings are 0.023 (4) and 0.051 (4), 0.014 (5) and 0.039 (4), and 0.004 (4) and 0.005 (5) Å, respectively. As stated above, there exist three possible isomers of 3-bpo, and the *cis*-I conformation was observed in this case. The non-bonding separation of the two pyridyl N donors (N3···N4) is 7.788 (5) Å. The angle between the center of the oxadiazole ring and the two N donors of the 3-pyridine ring is 110.5 (4)°. Bond lengths and angles agree with accepted values; full details are given in the archived CIF.

Analysis of the crystal packing of (I) showed the existence of three types of hydrogen-bonding interactions (N—H···N, C—H···O and C—H···N; Fig. 2 and Table 1), which connect the cations and anions into a three-dimensional network. The classical N3—H3···N4^{i} [symmetry code: (i) $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$] intermolecular hydrogen bonds between adjacent $C_{12}H_9N_4O^+$ cations link them into a one-dimensional zigzag

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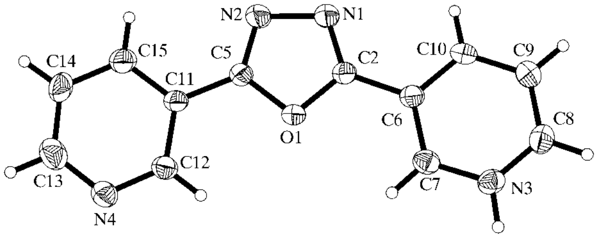

Figure 1
A view of the protonated cation in (I), shown with displacement ellipsoids at the 30% probability level.

chain. Furthermore, pyridinio atom H10 forms an intermolecular C10—H10···N1^{ii} [symmetry code: (ii) $-x+2$, $-y+2$, $-z+1$] bond with atom N1 of the oxadiazole ring in an adjacent cation, and thus a pair of such head-to-tail hydrogen bonds connect two adjacent cations into a dimer. The resulting motif, *C*, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter, 1990), is characterized as $N_2 = R_2^2(10)$. Such a hydrogen-bonding dimer can actually act as a four-connected node through four strong N3—H3···N4 hydrogen-bonding interactions, as stated above, resulting in a two-dimensional layered architecture. Meanwhile, two perchlorate anions located at the terminal position of each dimer form two close hydrogen-bonding graph-set motifs [*B* and *B*′; $N_3 = R_3^3(14)$] *via* intermolecular C8—H8···O3^{iii} [symmetry code: (iii) $-x+\frac{3}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$] and C15—H15···O5^{iv} [symmetry code: (iv) $x+\frac{1}{2}$, $-y+\frac{3}{2}$, $z-\frac{1}{2}$] interactions, as well as the above-mentioned C10—H10···N1 bonds. In addition, the two-dimensional hydrogen-bonded layers are expanded to a three-dimensional hydrogen-bonded supramolecular network by C12—H12···O2 interactions between the cations and anions from distinct hydrogen-bonded layers. Thus, through six hydrogen-bonding interactions (N3—H3···N4, C12—H12···O2 and C15—H15···O5), four cations and two anions are connected into a large new motif, *A* [$N_6 = R_6^6(36)$]. A three-dimensional hydrogen-bonded network has also been observed in the crystal structure of a related 3-pyridyl oxadiazole compound, namely 2-amino-5-(2-amino-3-pyridyl)-1,3,4-oxadiazole (Liszkiewicz *et al.*, 1999), which exhibits N—H···N interactions between the amine group and the oxadiazole/pyridyl rings. Examination of the structure of (I) with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids or π–π stacking interactions in the crystal lattice of (I).

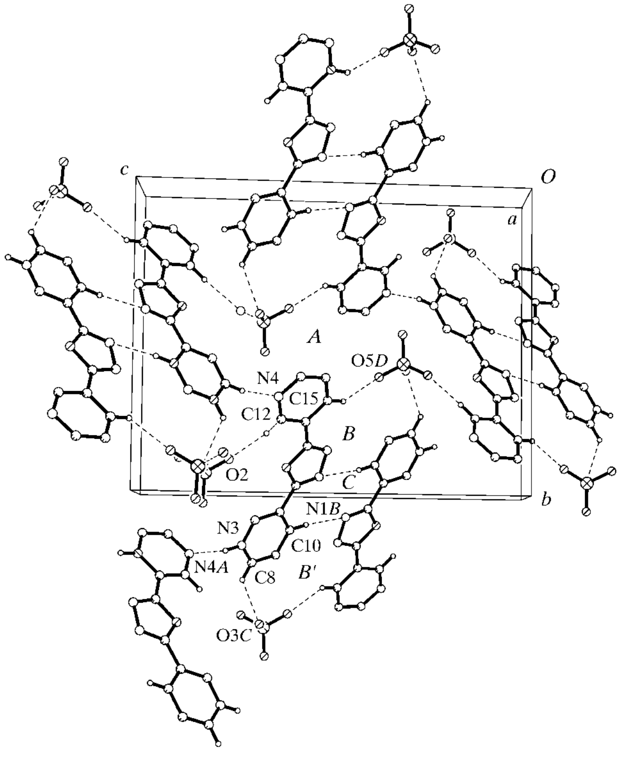

Figure 2
A view of part of the three-dimensional structure of (I), showing hydrogen-bonding interactions. Atom N4*A* is at ($-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$), atom N1*B* is at ($-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$), atom O3*C* is at ($-x+\frac{3}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$) and atom O5*D* is at ($x+\frac{1}{2}$, $-y+\frac{3}{2}$, $z-\frac{1}{2}$). The hydrogen-bonded rings *A*, *B*, *B*′ and *C* are defined in the *Comment*.

Experimental

Reaction of 3-bpo with $Mn(ClO_4)_2 \cdot 6H_2O$ (Lewis acid as proton-providing reagent) in a 1:1 molar ratio in CH_3CN/CH_3OH afforded colorless prismatic single crystals of (I) suitable for X-ray diffraction. Analysis calculated for $C_{12}H_9ClN_4O_5$: C 44.39, H 2.79, N 17.26%; found: C 44.68, H 2.61, N 17.08%.

Crystal data

$C_{12}H_9N_4O^+ \cdot ClO_4^-$
$M_r = 324.68$
Monoclinic, $P2_1/n$
$a = 5.4356\ (16)$ Å
$b = 13.992\ (4)$ Å
$c = 17.955\ (5)$ Å
$\beta = 96.382\ (5)^\circ$
$V = 1357.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.589$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5213 reflections
$\theta = 1.9$–25.0°
$\mu = 0.31$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.35 × 0.25 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Sheldrick, 1997)]
$T_{min} = 0.898$, $T_{max} = 0.926$
5507 measured reflections
2377 independent reflections
1286 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 25.0^\circ$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 16$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R(F) = 0.060$
$wR(F^2) = 0.155$
$S = 1.14$
2377 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

H atoms were visible in difference maps and were placed at calculated positions, with C—H distances of 0.93 Å and N—H distances of 0.90 Å, and refined as riding atoms, with isotropic

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N3—H3$\cdots$N4^{i}	0.86	1.85	2.701 (5)	169
C10—H10$\cdots$N1^{ii}	0.93	2.43	3.350 (5)	172
C8—H8$\cdots$O3^{iii}	0.93	2.55	3.232 (6)	131
C15—H15$\cdots$O5^{iv}	0.93	2.48	3.322 (7)	151
C12—H12$\cdots$O2	0.93	2.47	3.243 (6)	141

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

displacement parameters derived from the carrier atoms [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1713). Services for accessing these data are described at the back of the journal.

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