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The perchlorate salt of the novel diprotonated dinucleating ligand 1,3-bis{[2-(2-pyridinio)ethyl]-[2-(2-pyridyl)ethyl]amino}benzene

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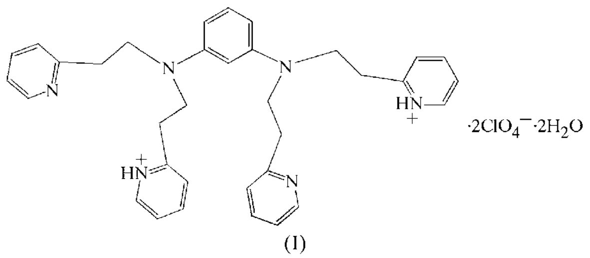
In the title salt, 1,3-bis{[2-(2-pyridinio)ethyl][2-(2-pyridyl)-ethyl]amino}benzene diperchlorate dihydrate, $C_{34}H_{38}N_6^{2+}\cdot 2ClO_4^-\cdot 2H_2O$, the cation contains two ethylpyridyl and two ethylpyridinium pendant pairs anchored to the two N atoms of 1,3-phenylenediamine. The pyridyl and pyridinium N atoms are flanked by a molecule of water through strong hydrogen-bonding interactions [N—H···O = 2.762 (6) and 2.758 (6) Å, and O—H···N = 2.834 (6) and 2.839 (6) Å]. The water molecules have weak hydrogen-bonding interactions with the perchlorate anions as well. One of the perchlorate anions is severely disordered.

Comment

Binucleating multidentate *N*,*O*-donor ligands, which can bind two metal ions in close proximity, have received considerable attention as synthetic models for the multinuclear metallo-biosites involved in many catalytic transformations (Tshuva & Lippard, 2004). The hexadentate ligand 1,3-tetrakis{[2-(2-pyridyl)ethyl]amino}benzene, PD (Murthy *et al.*, 1993), is one of these. An attempted synthesis of an iron(III)–oxo/hydroxo–acetato-bridged complex of PD by its reaction with ferric perchlorate, $Fe(ClO_4)_3.10H_2O$, acetic acid and triethylamine (1:2:2:2 ratio) in ethanol gave a pale-yellow crystalline solid, at first thought to be an Fe complex. An X-ray diffraction study showed that the product did not contain Fe but was the title compound, $PDH_2^{2+}\cdot 2ClO_4^-\cdot 2H_2O$, (I), in which the two pyridyl groups, one on each amino N atom, are protonated. The selective protonation of these, as opposed to the aromatic ring-substituted amine N atoms, suggests that they are more basic, as expected. A similar protonated salt of a tetradentate aminoethylpyridyl ligand formed under identical reaction conditions has been reported previously (Britton *et al.*, 1991). It is of interest that hydrogen-bonded tertiary aminopyridyl compounds are found to be antidotes for poisoning by organophosphorus compounds (Takeshi *et al.*, 2002).



(I)

A view of the hydrogen-bonded structure of (I) and its atom-numbering scheme is shown in Fig. 1. The structure includes a PDH_2^{2+} dication, two perchlorate anions (one severely disordered) and two molecules of water. The packing diagram is given in Fig. 2. Compound (I) has two aromatic ring-substituted amine N atoms (N1 and N4) and four pyridyl N atoms (N2, N3, N5 and N6), of which two pyridyl N atoms are protonated (H3N and H5N). The amino N atoms, N1 and N4, are planar; the angles around them are close to 120°, indicating a π-delocalization of their lone pairs with the benzene ring, which prevents their protonation or involvement in hydrogen bonds. In general, aminopyridyls are protonated in acidic solutions. In the present case, the protonation may be due to the acidic nature of the hydrated ferric perchlorate salt.

Notably, each pair of protonated pyridinium and non-protonated pyridyl groups trap a molecule of water (H_2O5 and H_2O6), one on each side, through strong hydrogen-bonding interactions (Table 1). The interactions are similar on both sides, with N3—H3N···O5 = 2.762 (6) and O5—H5*B*···N2 = 2.834 (6) Å, and N5—H5N···O6 = 2.758 (6) O6—H6*B*··· N6 = 2.839 (6) Å]. These water molecules also have additional weak hydrogen-bonding interactions with perchlorate anions. A subtle difference in their interaction is apparent, as atom

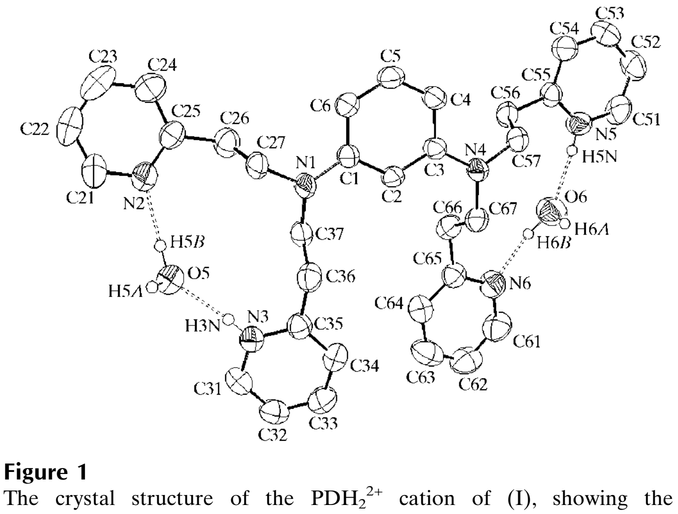


Figure 1
The crystal structure of the PDH_2^{2+} cation of (I), showing the intramolecular hydrogen bonding (dashed lines) and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity. The perchlorate anions are not shown.

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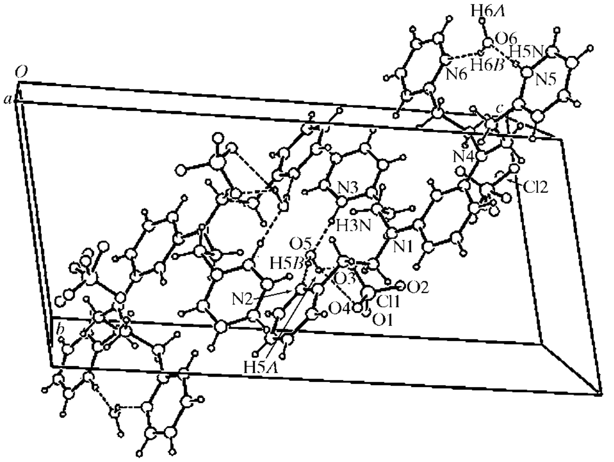

Figure 2
A partial packing diagram for (I). Disordered O-atom positions about Cl2 are shown. Selected atoms are labelled. Hydrogen bonds are shown as dashed lines.

H5*A* on O5 interacts with two O atoms, while atom H6*A* interacts with only one of the O atoms of the perchlorate anions (Table 1). These factors appear to have an effect on the relative orientations of the pyridyl and pyridinium rings. Rings N6/C61–C65 and N5/C51–C55, with stronger hydrogen-bonding interactions with perchlorate, deviate from coplanarity (dihedral angle = 28.2 °), while rings N2/C21–C25 and N3/C31–C35, with weaker perchlorate hydrogen-bonding interactions, are coplanar (dihedral angle = 1.76 °). By contrast, in another similar instance, a hexadentate ligand with methylpyridyl pendants (Buchen *et al.*, 1997), the two pyridine N atoms at each end of the molecule are mutually hydrogen bonded, with no intervening water molecule. The reason for the difference in compound (I) may be due to the longer arm length of the pendants allowing the accommodation of a molecule of water. These two examples clearly exemplify the key role of structure on the type and nature of hydrogen-bonding interactions.

The C—C and C—N bond distances in (I) are very close to the corresponding values reported for an analogous ligand system (Buchen *et al.*, 1997).

Experimental

The reaction of the binucleating ligand 1,3-tetrakis{[2-(2-pyridyl)-ethyl]amino}benzene, PD, and ferric perchlorate decahydrate, $Fe(ClO_4)_3\cdot10H_2O$, in the presence of acetic acid and triethylamine (1:2:2:2 molar ratio) in ethanol resulted in the formation of the title salt, (I), as pale-yellow needles in 86% yield. UV–vis [MeOH, λ_{max}, nm (ε, M^{-1} cm^{-1})]: 305 (632); IR (Nujol, cm^{-1}): 3488 (*s*, H_2O), 1100 (*s*, ClO_4^-); ^1H NMR (CD_3NO_2, 400 MHz): δ 3.42 (overlapping triplets, 8H, CH_2), 3.92 (overlapping triplets, 8H, CH_2py), 5.4 (*s*, *b*, –NH), 6.58 (*d*, 2H), 7.20 (*s*, 1H), 7.99–8.01 (*m*, 9H), 8.54 (*t*, 4H, 4-pyridyl), 8.68 (*d*, 4H, 6-pyridinium/pyridyl). Crystals suitable for X-ray diffraction were obtained from the original sample.

Crystal data

$C_{34}H_{38}N_6^{2+}\cdot2ClO_4^-\cdot2H_2O$
$M_r = 765.64$
Triclinic, $P\bar{1}$
$a = 9.264$ (4) Å
$b = 9.937$ (6) Å
$c = 20.751$ (8) Å
$\alpha = 78.28$ (4)°
$\beta = 87.01$ (3)°
$\gamma = 77.31$ (4)°
$V = 1824.6$ (15) Å^3

$Z = 2$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.24$ mm^{-1}
$T = 293$ (2) K
Needle, pale yellow
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.946$, $T_{max} = 1.000$
6833 measured reflections
6397 independent reflections
3517 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -24 \rightarrow 24$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.212$
$S = 1.02$
6397 reflections
518 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1022P)^2 + 1.7559P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3N···O5	0.95 (5)	1.82 (5)	2.762 (6)	170 (5)
N5—H5N···O6	0.85 (6)	1.91 (6)	2.758 (6)	172 (6)
O5—H5*B*···N2	0.90 (4)	1.95 (4)	2.834 (6)	172 (6)
O5—H5*A*···O3	0.90 (4)	2.32 (5)	2.996 (7)	132 (6)
O5—H5*A*···O4	0.90 (4)	2.33 (5)	3.123 (8)	147 (7)
O6—H6*A*···O10′^{i}	0.90	2.37	2.931 (10)	121
O6—H6*B*···N6	0.90 (4)	2.02 (4)	2.839 (6)	150 (7)

Symmetry code: (i) $x + 1, y - 1, z$.

H atoms attached to aromatic C atoms were fixed at C—H distances of 0.93 Å, while those attached to aliphatic methylene C atoms were fixed at C—H distances of 0.97 Å, and they were all refined using a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to the pyridyl N atoms (N3 and N5) were identified from difference maps and refined isotropically. The Fourier map gave a set of eight disordered positions for the O atoms of one of the perchlorate anions ($Cl2O_4^-$). Initially, four of those peaks satisfying nearly tetrahedral geometry were assigned as O atoms (O7, O8, O9 and O10) with partial site occupancy. Refinement, and hence the subsequent difference map, showed three more O-atom positions (O7′, O9′ and O10′). Thus, atom O8 was found common to two approximate tetrahedra. The constrained refinements were performed on these partial positions such that the atoms of the two tetrahedra remained in chemically meaningful positions. Two common occupancy factors were given to each disordered set with the sum constrained to 1. The H atoms of the two water molecules were located in a difference map and their positions were fixed during the refinement such that they remained in chemically meaningful positions. Both water molecules are hydrogen bonded to pyridine N atoms and perchlorate O atoms. Atom H6*A* of water molecule H_2O6, which is hydrogen bonded to the disordered perchlorate group $Cl2O_4^-$, is also disordered; its position was fixed at a geometrically meaningful position and was not refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995) in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) in *WinGX*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *WinGX*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1487). Services for accessing these data are described at the back of the journal.

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