organic compounds

Pyridoxinium picrate

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The title compound [systematic name: 3-hydroxy-4,5-bis-(hydroxymethyl)-2-methylpyridinium 2,4,6-trinitrophenolate], $C_8H_{12}NO_3^+ \cdot C_6H_2N_3O_7^-$, is a complex of picric acid with pyridoxine. The asymmetric part of the unit cell contains one pyridoxinium cation and one picrate anion. The aromatic rings of the picrate anion and the pyridoxinium cation are inclined with a dihedral angle of 83.19 (7)°. An intramolecular hydrogen bond between OH and a nearby CH_2OH group is observed in the cation. The hydrophobic layers at $y = \frac{1}{2}$ are packed between the hydrophilic layers at $y = 0$.

Comment

Vitamin B6, also known as pyridoxine, is one of the B group vitamins and is water soluble. It is required for both mental and physical health. Pyridoxine is one of the most versatile enzyme cofactors that support amino acid metabolism. It controls the absorption, metabolism and conversion of amino acids into neurotransmitters, antibodies, digestive enzymes, muscles and tissues in the body. Pyridoxal phosphate is a cofactor in the metabolism of amino acids and neurotransmitters and in the breakdown of glycogen. Pyridoxal phosphate can bind to steroid hormone receptors and may have a role in regulating steroid hormone action. Pyridoxal phosphate can be converted to pyridoxamine phosphate, which can also serve as an enzyme cofactor (Leklem, 1990). Pyridoxine has been found to play an essential role in the nervous system and aids in the metabolism of fats, carbohydrates and proteins. Other forms of vitamin B6 include pyridoxal and pyridoxamine.

(I)
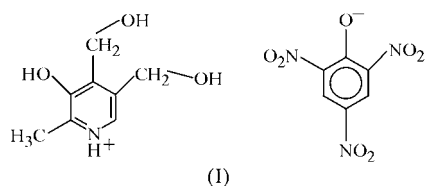
The crystal structures of pyridoxine (Longo *et al.*, 1982), pyridoxinium chloride (Bacon & Plant, 1980), pyridoxamine monohydrochloride (Longo & Richardson, 1980), copper

complexes of neutral pyridoxamine (Franklin & Richardson, 1980), *cis*-oxalatobis(pyridoxine)palladium(II) (Dey *et al.*, 2003), 6-dimethylaminopyridoxine-α^4-(*tert*-butyldimethylsilyl ether) (Culbertson *et al.*, 2003) and aquabis(2-methyl-4,5-bis(hydroxymethyl)pyridinium-3-oxalato)dioxouranium dichloride (Bonfada *et al.*, 2005) are already known. In the present work, the crystal structure of pyridoxinium picrate, (I), is reported.

The asymmetric part of the unit cell contains one pyridoxinium cation and one picrate anion (Fig. 1). The bond distances and angles are similar to those observed in other vitamin B6 compounds (Bacon & Plant, 1980). The protonation of the pyridine N atom is confirmed by the bond distances and angles, as in other pyridoxine complexes. Generally, in all the structures so far determined, vitamin B6 exists as a zwitterion in which the phenolic group is deprotonated and the pyridine N atom is protonated (Longo & Richardson, 1980). In the present structure, both the phenolic group and the pyridine N atom are protonated, as in pyridoxinium chloride (Bacon & Plant, 1980). In both CH_2OH groups, the OH group is symmetric with CH_2, as evident from the dihedral angles. Both CH_2OH groups are twisted from the plane of the pyridine ring, but the phenolic group is coplanar. The angle between the picrate and pyridoxine rings is 83.19 (7)°. The
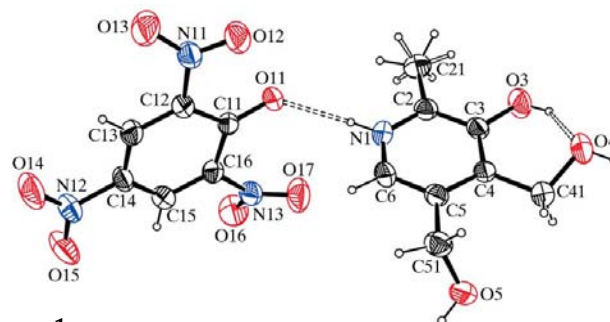
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.
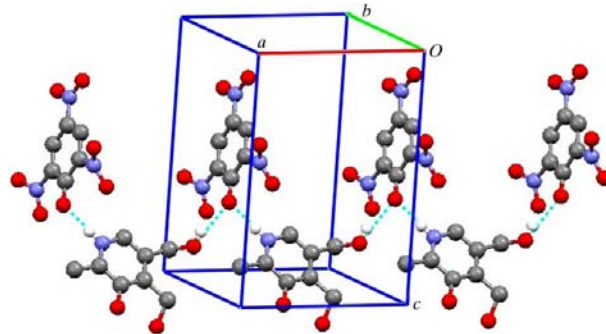
Figure 2
An infinite chain, connecting anions with cations, running along the *a* axis. H atoms not involved in hydrogen bonding have been omitted.
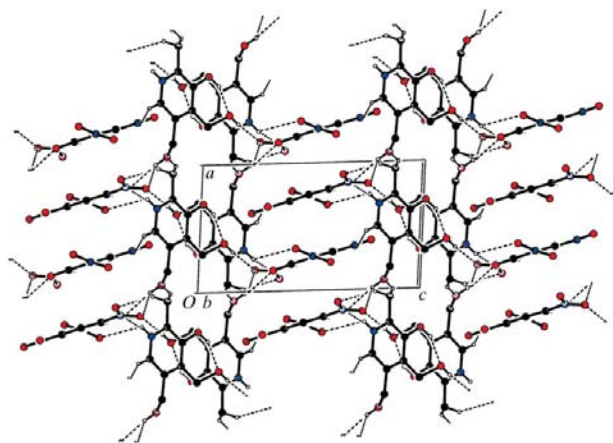
Figure 3
A packing diagram for (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

cations are linked to the picrate anions by an extensive hydrogen-bonding network.

The loss of a proton in the picrate anion is confirmed by the C—C distances near the phenolic group (C11—C12 and C11—C16). The picrate anion plays a vital role in forming hydrogen bonds with the pyridoxinium residue. The anion forms a strong asymmetric O—H···O hydrogen bond and an N—H···O hydrogen bond with the pyridoxinium residue. Of the three nitro groups, two (N1/O2/O3 and N3/O6/O7) are twisted from the plane of the ring. This twisting does not depend upon the C—N bond distances (Soriano-Garcia *et al.*, 1978); the torsion angles are shown in Table 1. The picrate anions are stacked nearly parallel to the *bc* plane, making an angle of 15.86° with the *bc* plane. Intermolecular N1—H1···O11 and O5—H5···O11/O12 hydrogen bonds link pairs of picric acid molecules through O and NO$_2$ groups (Table 2). In addition to the hydrogen bonds, intramolecular contacts between phenolic O atoms and nitro groups are observed. These are the important features observed in all aromatic picrate complexes.

The pyridine N and O5 atoms form bifurcated hydrogen bonds with picrate anions, thus forming an infinite chain running along the *a* axis (Fig. 2). An intramolecular hydrogen bond between OH and a nearby CH$_2$OH group is observed, with graph-set motif $R_1^1(6)$ (Etter *et al.*, 1990). The pyridoxinium cation forms a closed dimer with an inversely related cation *via* C—H···O and O—H···O hydrogen bonds. The cation also forms a head-to-tail sequence with inversely related cations through picrate anions *via* N—H···O and O—H···O hydrogen bonds. The hydrophobic layers at $y = \frac{1}{2}$ are packed between the hydrophilic layers at $y = 0$ (Fig. 3).

Experimental

The title compound, (I), was crystallized from an aqueous solution of pyridoxinium chloride and picric acid in a 1:1 stoichiometric ratio at room temperature by slow evaporation.

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.333 (3)	C11—O11	1.258 (3)
N1—C2	1.342 (3)		
C6—N1—C2	124.4 (2)	O11—C11—C12	125.0 (2)
O11—C11—C16	123.7 (2)	C16—C11—C12	111.2 (2)
N1—C2—C3—O3	179.7 (2)	C4—C5—C51—O5	−62.6 (3)
C21—C2—C3—O3	0.2 (3)	C11—C12—N11—O12	22.2 (4)
O3—C3—C4—C5	179.3 (2)	C13—C12—N11—O13	24.7 (3)
O3—C3—C4—C41	−1.7 (3)	C13—C14—N12—O14	−1.7 (4)
C3—C4—C41—O4	35.1 (3)	C15—C14—N12—O15	−0.5 (4)
C5—C4—C41—O4	−145.9 (2)	C11—C16—N13—O17	−39.1 (3)
C6—C5—C51—O5	117.9 (2)	C15—C16—N13—O16	−35.4 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O11	0.86	2.01	2.797 (2)	152
O3—H3$\cdots$O4	0.82	1.87	2.572 (3)	143
O4—H4$\cdots$O12^i	0.82	2.05	2.862 (3)	174
O5—H5$\cdots$O11^{ii}	0.82	2.01	2.779 (2)	157
C21—H21$B\cdots$O12^{iii}	0.96	2.70	3.472 (3)	138
C21—H21$F\cdots$O13^{iii}	0.96	2.49	3.348 (3)	148
C6—H6$\cdots$O14^{iv}	0.93	2.40	3.217 (3)	147

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

All H atoms were placed in geometrically calculated positions and included in the refinement in the riding–model approximation, with O—H = 0.82 Å, C—H = 0.93–0.96 Å and N—H = 0.86 Å, and with U_{iso}(H) = 1.2–1.5U_{eq} of the carrier atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC*

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3016). Services for accessing these data are described at the back of the journal.

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