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Diphenylboron chelate of a pyridoxal hemiacetal with ethanol

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Key indicators

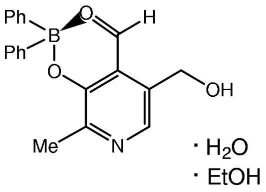
Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.137
Data-to-parameter ratio = 21.5

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

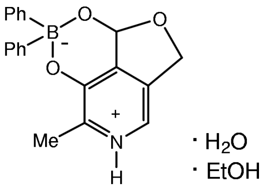
The title compound, 4-ethoxy-5-(hydroxymethyl)-8-methyl-2,2-diphenyl-1,3-dioxa-7-azonia-2-borata-1,2,3,4-tetrahydronaphthalene monohydrate, $C_{22}H_{24}BNO_4 \cdot H_2O$, contains a six-membered BOCCCO heterocycle with a half-chair conformation, fused to a pyridine ring. An N—H···O hydrogen bond is formed between the protonated pyridine ring and the associated water molecule, and two O—H···O hydrogen bonds are formed using the water H atoms. The hydroxyl H atom is involved in an O—H···π interaction. The residues are thus linked to form ribbons parallel to the a axis.

Comment

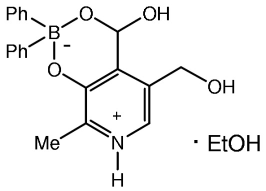
Pyridoxal has been found by X-ray crystallography to exist in the solid state as a cyclic hemiacetal, involving the aldehyde and the hydroxymethyl group (Rao *et al.*, 1982; MacLaurin & Richardson, 1985). In the course of our investigations on the boron chelate formation of pyridoxal and derivatives (Barakat, 2002; Barakat & Kliegel, unpublished results), we reacted diphenylborinic acid (anhydride) with pyridoxal in ethanol. The elemental analysis and spectroscopic features of the resulting crystalline compound were consistent with the diphenylborinate of pyridoxal, but containing additionally both 1 mol of H_2O and 1 mol of EtOH. Drying of the substance in vacuo for several hours at 330 K did not remove these.



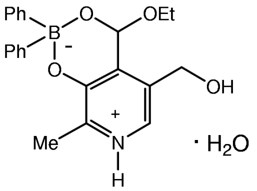
(I)



(II)



(III)



(IV)

Since the molecular structure (I) (see scheme) with an intact aldehyde function could be excluded by analysis of the IR and ^{1}H NMR spectra, the acetalic structure alternatives (II)–(IV) had to be considered. The cycloacetal form (II),

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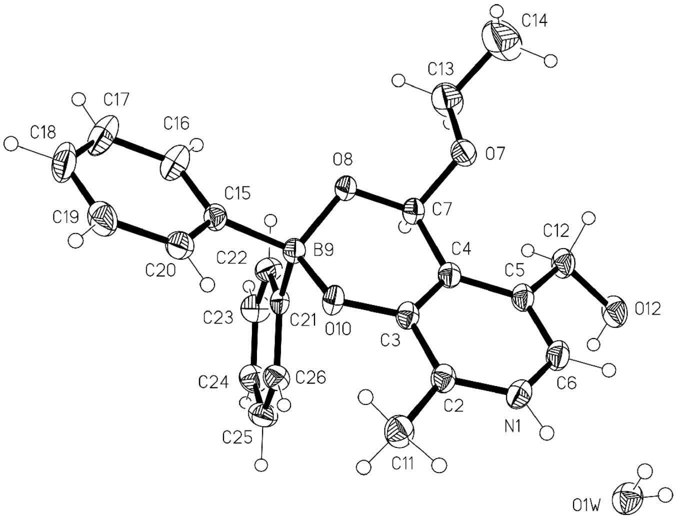

Figure 1
The structure of compound (IV) in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary.

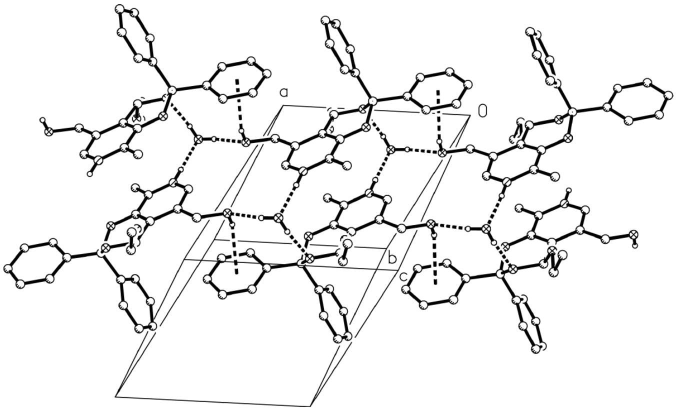

Figure 2
Packing of compound (IV), showing hydrogen bonds as dashed lines. H atoms not involved in classical or O—H$\cdots\pi$ hydrogen bonding (see text) have been omitted for clarity.

which could be expected as the diphenylboron derivative of the solid-state hemiacetal form of pyridoxal, seemed, however, somewhat improbable because of the absence of a typical *AB* quartet ^{1}H NMR signal for the endocyclic O—CH$_2$—C methylene group. An unambiguous distinction between the acetalic forms (III) and (IV) could not be achieved by spectroscopic means. Thus, an X-ray crystallographic analysis was carried out to determine unambiguously the molecular structure (IV) for the solid state.

The structure of (IV) is shown in Fig. 1. In (IV), a diphenylboron chelate is formed by the pyridoxal ethanol hemiacetal as a bidentate ligand, and the molecule is associated with one molecule of water of crystallization.

The six-membered BOCCCO ring shows, consistent with the approximately planar O10—C3—C4—C7 moiety [torsion angle = 2.9 (2)°], a half-chair form (Bucourt & Hainaut, 1965) with atom B9 lying 0.415 (2) Å to one side and O10 0.307 (2) Å to the opposite side of the plane defined by the other four atoms (r.m.s. deviation = 0.009 Å). The geometry at boron is close to tetrahedral. The two B—O bond lengths differ by 0.03 Å, with the shorter B9—O8 bond [1.4941 (17) Å] involving the carbonyl O atom and the B9—O10 bond [1.5244 (17) Å] involving the phenolic O atom of pyridoxal. One phenyl ring adopts a (pseudo-)axial and the other an equatorial position, whereby the former has a somewhat longer B—C bond [B9—C21 = 1.627 (2) Å *versus* B9—C15 = 1.612 (2) Å], a general trend observed also in other diphenylboron complexes of this type (Kliegel *et al.*, 1993, and references therein; Kliegel *et al.*, 1997).

The B,N-betainic bicycle is linked to the water within the asymmetric unit by an N—H$\cdots$O hydrogen bond from the protonated pyridine moiety. Both water H atoms act as hydrogen-bond donors to atoms O8 and O12 of two different neighbouring molecules (Table 2). However, the hydroxy H atom at O12 is not involved in classical hydrogen bonding; it acts instead as donor for an O—H$\cdots\pi$ interaction to the centroid (Cent) of ring C15–C20, with dimensions O—H = 0.81 (2) Å, H$\cdots$Cent = 2.52 Å and O—H$\cdots$Cent = 153°. The net effect is to form ribbons of molecules parallel to the *a* axis, in planes parallel to (101) (Fig. 2). Two C—H$\cdots$O interactions (Table 2) may be regarded as playing a subordinate role in the packing.

Experimental

Pyridoxal hydrochloride (0.61 g, 3 mmol) was suspended/dissolved in 5 ml of ethanol (50%) and mixed with oxybis(diphenylborane) (0.52 g, 1.5 mmol) and triethylamine (0.3 g, 3 mmol) in 2 ml of ethanol with brief heating to the boiling point. Cooling (and addition of a small amount of water, if necessary) yielded 0.79 (67%) of colourless crystals (m.p. 409 K, from 50% ethanol/water). Single crystals suitable for X-ray crystallography were obtained by slow crystallization from ethanol and water (1:1). IR (KBr): 3460 (O—H), 1638/1595 cm^{-1} (C═N/C═C). ^{1}H NMR (90 MHz, DMSO–TMS): δ 1.08 (*t, J* = 9 Hz, C—O—C—CH$_3$), 2.61 (*s*, CH$_3$), 3.46 (*q, J* = 9 Hz, C—O—CH$_2$), 4.50 (*s*, pyr-CH$_2$—O), 4.96 (broad, exchangeable, OH), 5.69 (*s*, O—CH—O), 6.85–7.50 (*m*, 10 aromatic H), 7.79 (*s*, 1 aromatic H); ^{11}B NMR (64 MHz, DMSO–Et$_2$OBF$_3$): δ 3.8. Analysis calculated for C$_{22}$H$_{26}$BNO$_5$: C 68.26, H 6.92, B 2.56, N 3.31%; found: C 68.03, H 6.82, B 2.55, N 3.35%. The compound gives a blue colour reaction with diphenylcarbazone in methanol, indicating the presence of a diphenylboron moiety (Neu, 1960; Friese & Umland, 1978).

Crystal data

$C_{22}H_{24}BNO_4\cdot H_2O$
$M_r = 395.25$
Triclinic, $P\overline{1}$
$a = 9.2511$ (12) Å
$b = 10.1801$ (12) Å
$c = 12.447$ (2) Å
$\alpha = 88.243$ (3)°
$\beta = 72.656$ (3)°
$\gamma = 70.188$ (3)°
$V = 1049.4$ (3) Å^3
$Z = 2$
$D_x = 1.251$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 4093 reflections
$\theta = 2.5$–30.4°
$\mu = 0.09$ mm^{-1}
$T = 133$ (2) K
Tablet, colourless
0.40 × 0.23 × 0.11 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
12 174 measured reflections
6031 independent reflections
4138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 30.0$°
$h = -12 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.137$
$S = 1.03$
6031 reflections
280 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

B9—O8	1.4941 (17)	B9—C15	1.6119 (19)
B9—O10	1.5244 (17)	B9—C21	1.627 (2)
O8—B9—O10	107.49 (10)	O8—B9—C21	110.79 (10)
O8—B9—C15	109.86 (10)	O10—B9—C21	108.59 (10)
O10—B9—C15	107.61 (10)	C15—B9—C21	112.32 (10)
O10—C3—C4—C7	2.86 (19)	C7—O8—B9—O10	61.10 (13)
C3—C4—C7—O8	11.69 (16)	C4—C3—O10—B9	15.25 (17)
C4—C7—O8—B9	−44.49 (14)	O8—B9—O10—C3	−44.66 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O1*W*	0.890 (17)	1.829 (18)	2.7010 (16)	166.0 (16)
O1*W*—H02···O8^{i}	0.81 (2)	1.95 (2)	2.7527 (14)	170.0 (19)
O1*W*—H03···O12^{ii}	0.85 (2)	1.95 (2)	2.7864 (15)	167.2 (19)
C11—H11*C*···O7^{i}	0.98	2.58	3.3122 (17)	132
C24—H24···O1*W*^{iii}	0.95	2.61	3.4398 (18)	146

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

The NH and OH H atoms were refined freely. Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups (C—H = 0.98 Å and H—C—H = 109.5°) Other H atoms were included using a riding model with fixed C—H bond lengths (Å) of 0.95 (sp^2 CH), 0.99 (sp^3 CH) or 1.00 (CH_2). $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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