

4,4'-Bipyridine dihydrate at 130 K

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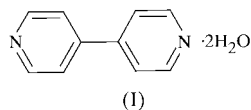
Received 25 September 2000

Accepted 23 October 2000

The 4,4'-bipyridine molecules in the title compound, $C_{10}H_8N_2 \cdot 2H_2O$, are stacked in the direction of the crystallographic b axis. These stacks are connected *via* $O-H \cdots N$ and $O-H \cdots O$ hydrogen bonds to form sheets which lie parallel to (100). Chains of $O-H \cdots O$ hydrogen-bonded water molecules are located between the bipyridine stacks. Altogether, four crystallographically independent water molecules and two crystallographically independent bipyridine molecules are involved.

Comment

The title compound, (I), was obtained as a by-product in the preparation of new coordination polymers under hydrothermal conditions. Whereas the crystal structure of anhydrous 4,4'-bipyridine is known (Boag *et al.*, 1999), no structure of a hydrated form has been reported so far.



In the crystal structure of (I), the 4,4'-bipyridine molecules are stacked in the direction of the crystallographic b axis (Fig. 1*a*). There are two different stacks, each built up of one of the two crystallographically independent 4,4'-bipyridine molecules. Within the stacks, each of the two six-membered rings of neighbouring molecules

are stacked perfectly on each other and are always parallel. The distances between the centres of neighbouring rings are 3.70 (1) and 3.74 (1) Å in one stack (C1–C10), and 3.71 (1) and 3.72 (1) Å in the other stack (C11–C20). Between the stacks are channels in which the water molecules are located.

The water molecules are connected *via* $O-H \cdots O$ hydrogen bonds to form two crystallographically independent chains parallel to the b axis, each built up of two crystallographically independent water molecules (Fig. 1*b*). Within the chains, the O atom of each water molecule acts as an acceptor for a hydrogen bond from a neighbouring water molecule, and as a donor through one H atom to a 4,4'-bipyridine molecule and through the other H atom to the next neighbouring water molecule (details in Table 1). The interactions between the water and the 4,4'-bipyridine molecules lead to 4,4'-bipyridine $\cdots H_2O \cdots H_2O \cdots$ 4,4'-bipyridine chains, which proceed in the direction of the c axis. The combination of all these hydrogen-bonding interactions results in the formation of sheets which lie parallel to (100).

The two crystallographically independent 4,4'-bipyridine molecules in the asymmetric unit have similar geometrical parameters. The six-membered rings are twisted by 41.6 (1)° in both molecules. This value is similar to that of 37.2° determined for 4,4'-bipyridine in the gas phase (Almenningen & Bastiansen, 1958) and corresponds closely with the value of

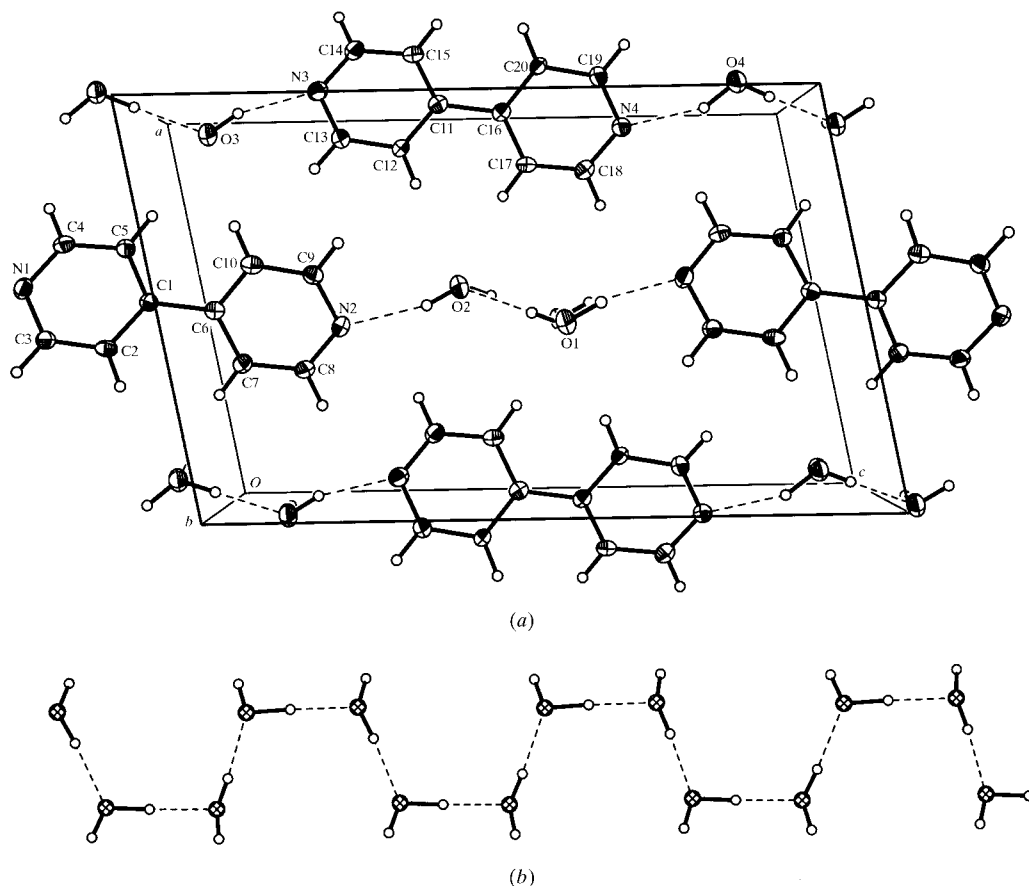


Figure 1

(a) The crystal structure of (I) with the atom-labelling scheme, viewed along the b axis. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown as dotted lines. H atoms are drawn as small spheres of arbitrary radii. (b) A view of the chains formed in (I) by the water molecules.

48.6° obtained from theoretical calculations (Ould-Moussa *et al.*, 1996). In contrast, in the structure of anhydrous 4,4'-bipyridine, which also exhibits two crystallographically independent molecules in the asymmetric unit, these angles amount to 18.5 (1) and 34.9 (1)° (Boag *et al.*, 1999). All other geometrical parameters are similar to those in the anhydrous structure of 4,4'-bipyridine (Boag *et al.*, 1999).

Experimental

Compound (I) was obtained as a by-product in the reaction of PbCl₂, 4,4'-bipyridine (ACROS) and squaric acid (ACROS) in the ratio 1:4:1 in water under hydrothermal conditions using a Teflon-lined steel autoclave. The reaction mixture was heated at 423 K for 1 d and cooled to room temperature at 1 K min⁻¹. The precipitate was filtered off and the residue consisted of colourless needles of (I) as the major phase and only a few colourless blocks of a second phase which it has not yet been possible to identify. Compound (I) decomposes in air within a few hours, leading to a white powder of 4,4'-bipyridine which is amorphous under X-ray powder diffraction.

Crystal data

C ₁₀ H ₈ N ₂ ·2H ₂ O	$D_x = 1.302 \text{ Mg m}^{-3}$
$M_r = 192.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 5270 reflections
$a = 9.1333 (7) \text{ \AA}$	$\theta = 3\text{--}26^\circ$
$b = 7.4310 (4) \text{ \AA}$	$\mu = 0.092 \text{ mm}^{-1}$
$c = 14.7171 (12) \text{ \AA}$	$T = 130 (2) \text{ K}$
$\beta = 101.052 (9)^\circ$	Needle, colourless
$V = 980.32 (12) \text{ \AA}^3$	$0.50 \times 0.06 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS diffractometer	$\theta_{\text{max}} = 25.96^\circ$
φ scans	$h = -11 \rightarrow 10$
7618 measured reflections	$k = -9 \rightarrow 8$
2044 independent reflections	$l = -18 \rightarrow 18$
1278 reflections with $I > 2\sigma(I)$	Intensity decay: negligible
$R_{\text{int}} = 0.043$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$
$wR(F^2) = 0.126$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.017$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2044 reflections	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
253 parameters	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

H atoms bound to C were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model, with C—H = 0.95 Å. The water H atoms were initially located in a difference map; however, this resulted in some excessively large O—H distances. Free refinement of the water H atoms or with restrained O—H bond lengths always yielded a poor O—H geometry. Therefore, the coordinates of the H atoms from the difference map were recalculated to give O—H distances of 0.90 Å and the atoms

Table 1

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H11O \cdots N1 ⁱ	0.90	1.99	2.839 (4)	157
O1—H21O \cdots O2	0.90	1.84	2.735 (4)	176
O2—H12O \cdots N2	0.90	1.99	2.866 (4)	164
O2—H22O \cdots O1 ⁱⁱ	0.90	1.88	2.783 (6)	178
O3—H13O \cdots N3	0.90	1.99	2.829 (4)	155
O3—H23O \cdots O4 ⁱⁱⁱ	0.90	1.85	2.748 (4)	174
O4—H14O \cdots N4	0.90	2.01	2.874 (5)	162
O4—H24O \cdots O3 ^{iv}	0.90	1.90	2.784 (7)	167

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

were refined with fixed isotropic displacement parameters using a riding model. The origin was fixed by floating-origin restraints (Flack & Schwarzenbach, 1988). Because no heavy atom was present, the absolute structure could not be determined; therefore, all Friedel equivalents measured were merged. The observed reflection conditions are in agreement with the centrosymmetric space group $P2_1/n$, but the structure cannot be solved in this space group. In addition, the structures of both independent molecules are very similar. However, a detailed analysis of the crystal structure shows that the correct space group is $P2_1$ and that the structure is pseudo-centrosymmetric.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

This work is supported by the state of Schleswig–Holstein. We are very grateful to Professor Dr Wolfgang Bensch for the use of his experimental equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1112). Services for accessing these data are described at the back of the journal.

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