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Pyridoxamine Monohydrochloride†

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(*Received* 17 *March* 1980; *accepted* 8 *May* 1980)

Abstract. $C_8H_{13}N_2O_2^+.Cl^-$, M_r = 204·7, monoclinic, space group $P2/c$, a = 7·893 (1), b = 9·057 (1), c = 13·507 (1) Å, β = 96·95 (2)°, Z = 4, D_c = 1·418 Mg m^{-3}, R = 0·058 for 1515 reflections with $|F_o| \geq 3\sigma(F_o)$. The pyridoxamine cations HPM$^+$ have a deprotonated phenolic group and protonated ring and amino N atoms. The cations are linked to the Cl$^-$ anions by an extensive hydrogen-bonding network.

Introduction. The crystal structure of pyridoxamine hydrochloride, HPM$^+$Cl$^-$, has been determined as part of our research on the structures and spectra of vitamin B$_6$ derivatives (K. J. Franklin & Richardson, 1978, 1980; T. A. Franklin & Richardson, 1980; Thompson, Balenovich, Hornich & Richardson, 1980). The infrared spectrum of HPMCl suggested that the stable tautomer of HPM$^+$ was one in which the phenolic group was ionized and the pyridine ring and amino group were protonated (T. A. Franklin & Richardson, 1980). This has been confirmed by the present crystal structure determination.

The crystals were prepared by evaporation of an aqueous equimolar solution of PM.2HCl and NaOH. Weissenberg photographs showed the absence of 0*k*0 reflections for *k* odd and *h*0*l* reflections for *l* odd, uniquely establishing the space group as $P2/c$. A single crystal was aligned about the a^* axis on a manual Picker diffractometer, and cell dimensions were determined with Zr-filtered Mo $K\alpha_1$ radiation (λ = 0·70926 Å). Data were collected by ω–2θ scans over a 2θ range of 2° at a rate of 1° min^{-1}. 10 s backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–50 reflections, and did not vary significantly during the data collection. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No absorption correction was made (μ = 0·372 mm^{-1}).

An E map revealed the non-hydrogen atoms, whose positions were refined by full-matrix least squares using the *SHELX* set of programs (Sheldrick, 1976). Scattering factors for neutral C, H, N, O, and Cl atoms were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, F_o and F_c are the observed and calculated structure factors, $w = [\sigma^2(F_o) + 0{\cdot}001\ F_o^2]^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-hydrogen atoms were given anisotropic temperature factors. Positional parameters were refined for the five H atoms whose positions were not fixed geometrically [H(1),H(7), H(8),H(9),H(12)]. The H(2), H(3), and H(4) atoms were refined as part of a rigid methyl group. The positions of the other H atoms were calculated with $r_{\text{C–H}}$ = 1·08 Å. All H atoms were assigned isotropic thermal parameters U of 0·04 Å^2.

A total of 1700 reflections with $2\theta \leq 50°$ were measured of which 1515 had $|F_o| \geq 3\sigma(F_o)$ and were classified as observed. The weighted residual, $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$, was 0·063. There were no significant features on the final difference map.

The atomic positional parameters are presented in Table 1, and the numbering scheme is shown in Fig. 1.§

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† 4-Aminomethyl-3-hydroxy-5-hydroxymethyl-2-methylpyridine hydrochloride.

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§ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35328 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic parameters for pyridoxamine hydrochloride* ($\times 10^4$ *for* C, O, N, *and* Cl, $\times 10^3$ *for* H)

Estimated standard deviations are given in parentheses. The asterisks indicate H atoms whose positions were calculated.

	x	y	z	U_{eq} (Å^2)
Cl	5595 (1)	3297 (1)	3195·8 (7)	386
N(1)	3077 (3)	5765 (3)	389 (2)	277
N(2)	1497 (4)	2020 (4)	−2202 (2)	304
O(1)	2096 (3)	978 (3)	1089 (2)	413
O(2)	374 (3)	4901 (3)	−1845 (2)	335
C(1)	3490 (4)	4440 (4)	783 (2)	303
C(2)	2878 (4)	3176 (4)	288 (2)	264
C(3)	1778 (4)	3339 (3)	−604 (2)	239
C(4)	1354 (4)	4750 (4)	−1008 (2)	242
C(5)	2087 (4)	5998 (4)	−481 (2)	256
C(6)	3469 (4)	1708 (4)	702 (3)	322
C(7)	973 (4)	2043 (4)	−1174 (2)	311
C(8)	1831 (4)	7545 (4)	−853 (3)	339
H(1)	339 (5)	652 (5)	72 (3)	
H(2)	109	745	−158	
H(3)	302	809	−93	
H(4)	113	818	−36	
H(5)*	−40	213	−122	
H(6)*	138	103	−79	
H(7)	86 (5)	140 (5)	−252 (3)	
H(8)	270 (5)	185 (4)	−223 (3)	
H(9)	138 (5)	294 (5)	−251 (3)	
H(10)*	451	186	129	
H(11)*	390	104	12	
H(12)	250 (5)	32 (5)	132 (3)	
H(13)*	430	436	149	

Table 2. *Bond distances* (Å) *and angles* (°) *for pyridoxamine hydrochloride, with e.s.d.'s in parentheses*

N(1)–C(1)	1·337 (4)	C(7)–N(2)	1·497 (4)
C(1)–C(2)	1·383 (5)	C(4)–O(2)	1·298 (4)
C(2)–C(3)	1·405 (4)	C(5)–C(8)	1·493 (5)
C(3)–C(4)	1·414 (4)	N(1)–H(1)	0·84 (4)
C(4)–C(5)	1·420 (4)	N(2)–H(7)	0·84 (4)
C(5)–N(1)	1·347 (4)	N(2)–H(8)	0·97 (4)
C(2)–C(6)	1·495 (4)	N(2)–H(9)	0·93 (4)
C(6)–O(1)	1·422 (4)	O(1)–H(12)	0·73 (4)
C(3)–C(7)	1·502 (4)		

N(1)–C(1)–C(2)	119·8 (3)	C(4)–C(5)–C(8)	123·2 (3)
C(1)–C(2)–C(3)	118·1 (3)	N(1)–C(5)–C(8)	118·7 (3)
C(1)–C(2)–C(6)	118·7 (3)	C(1)–N(1)–C(5)	125·1 (3)
C(3)–C(2)–C(6)	123·2 (3)	C(1)–N(1)–H(1)	118 (3)
C(2)–C(6)–O(1)	109·5 (3)	C(5)–N(1)–H(1)	117 (3)
C(2)–C(3)–C(4)	121·3 (3)	C(7)–N(2)–H(7)	106 (3)
C(2)–C(3)–C(7)	122·4 (3)	C(7)–N(2)–H(8)	115 (2)
C(4)–C(3)–C(7)	116·3 (3)	C(7)–N(2)–H(9)	113 (2)
C(3)–C(7)–N(2)	109·8 (3)	H(8)–N(2)–H(9)	100 (3)
C(3)–C(4)–C(5)	117·6 (3)	H(9)–N(2)–H(7)	111 (4)
C(3)–C(4)–O(2)	121·3 (3)	H(7)–N(2)–H(8)	114 (3)
C(5)–C(4)–O(2)	121·1 (3)	C(6)–O(1)–H(12)	103 (3)
C(4)–C(5)–N(1)	118·0 (3)		

Bond distances and angles are given in Table 2. The molecular packing is shown in Fig. 2, and hydrogen-bonding parameters are listed in Table 3.

Table 3. *Hydrogen bonding in pyridoxamine hydrochloride*

Symmetry superscripts: (i) $1-x, 0\cdot5+y, 0\cdot5-z$; (ii) $x, 0\cdot5-y, -0\cdot5+z$; (iii) $-x, -0\cdot5+y, -0\cdot5-z$; (iv) $1-x, -0\cdot5+y, 0\cdot5-z$.

X–H$\cdots Y$	$X\cdots Y$ (Å)	H$\cdots Y$ (Å)	Angle XHY (°)
N(1)–H(1)$\cdots$Cl^{i}	3·086	2·25	172
N(2)–H(7)$\cdots$O(2^{iii})	2·657	1·82	174
N(2)–H(8)$\cdots$Cl^{ii}	3·227	2·29	162
N(2)–H(9)$\cdots$O(2)	2·816	2·19	124
N(2)–H(9)$\cdots$O(1^{ii})	3·017	2·26	138
O(1)–H(12)$\cdots$Cl^{iv}	3·118	2·41	164

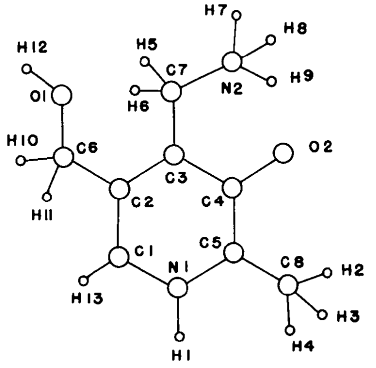

Fig. 1. Numbering scheme for HPM$^+$Cl$^-$.

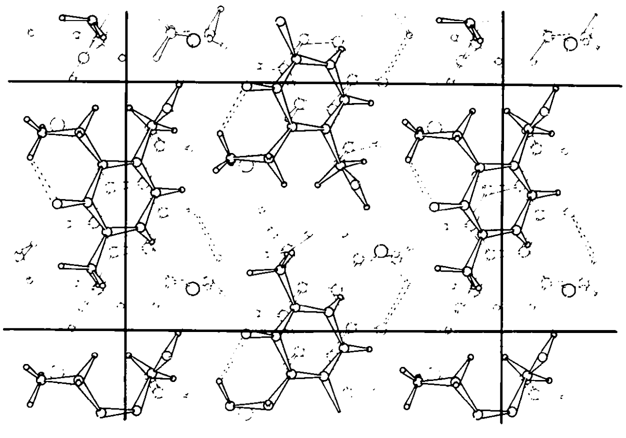

Fig. 2. Crystal structure viewed down **a**. The small circles represent H atoms; large circles represent Cl$^-$ ions.

Discussion. The bond distances and angles are similar to those observed in other vitamin B$_6$ derivatives (Hanic, 1966; K. J. Franklin & Richardson, 1978, 1980; Mosset, Nepveu-Juras, Haran & Bonnet, 1978; Thompson *et al.*, 1980). The bond angle at the pyridine N(1) is 125·1 (3)°, as has been observed for other compounds with a protonated ring N atom (Singh, 1965). The C(4)–O(2) distance of 1·298 (4) Å is 0·06 Å less than the corresponding distance in pyridoxine hydrochloride (Hanic, 1966), but is close to the values observed for vitamin B_6 compounds whose phenolic group is deprotonated (Mosset *et al.*, 1978; K. J. Franklin & Richardson, 1980; Thompson *et al.*, 1980). The pyridine ring is planar.

The $-CH_2NH_3^+$ group forms an intramolecular hydrogen bond to the phenolate oxygen O(2) (Table 3). The resulting ring, O(2)–C(4)–C(3)–C(7)–N(2)–H(9), has the same conformation as the metal chelate rings in the copper and zinc complexes of pyridoxamine (Thompson *et al.*, 1980; K. J. Franklin & Richardson, 1980). The H(9) atom in the $-CH_2NH_3^+$ group also makes a close contact with O(1) in a glide-related molecule, although the interaction seems to be somewhat weaker than the intramolecular one (Table 3).

The HPM^+ cations are stacked with the ring planes parallel (Fig. 2). The stacks are linked by hydrogen bonds from the ammonium group to the phenolate O atom O(2) in screw-related molecules (not shown in Fig. 2), and by hydrogen bonds from the ammonium, hydroxymethyl, and pyridinium groups to Cl^- ions (Table 3).

This research has been supported by the Natural Sciences and Engineering Research Council of Canada. The close attention paid to the data collection by Austin S. Wol is gratefully acknowledged.

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Acta Cryst. (1980). B**36**, 2458–2460

Benzotriazolium Hydrogensulphate

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(*Received* 28 *November* 1979; *accepted* 7 *May* 1980)

Abstract. $C_6H_6N_3^+.HSO_4^-$, M_r = 217·2, orthorhombic, *Pbcn*, a = 12·976 (1), b = 7·892 (1), c = 17·292 (1) Å, Z = 8, V = 1770·8 (3) Å^3, D_c = 1·63 Mg m^{-3}, F(000) = 896, Cu $K\alpha$ radiation (λ = 1·5418 Å), μ(Cu $K\alpha$) = 0·318 mm^{-1}. The structure was solved by the heavy-atom method and refined by full-matrix least squares. The final R and R_w for 1239 observed reflexions and 156 parameters are respectively 0·044 and 0·062. The benzotriazolium ions have *mm* symmetry. Two strong N–H···O hydrogen bonds, 2·687 (5) and 2·705 (5) Å, link the benzotriazolium cations to the hydrogensulphate anions, which, in turn, form infinite chains through an O–H···O hydrogen bond of 2·565 (5) Å.

Introduction. Deliquescent crystals of the title compound were obtained by evaporation to dryness on P_2O_5 of an aqueous solution of H_2SO_4 and benzotriazole. A prismatic crystal (0·09 × 0·14 × 0·46 mm), elongated along **b**, was sealed in a Lindemann capillary tube and used for data collection on an Enraf–Nonius four-circle CAD-4 diffractometer. Monochromatized Cu $K\alpha$ radiation was used. Lattice constants were obtained by least squares from the 2θ values of 25 reflexions. Of 1755 independent reflexions measured to $\sin\theta/\lambda \simeq$ 0·60 Å^{-1} by the ω–θ scan technique, 1239 having $I > 3\sigma(I)$ were taken as observed. During the data collection, the azimuth of each reflexion was adjusted to reach as close as possible the position of the minimum absorption path, so that no correction for absorption was applied. The intensities of three monitor reflexions, periodically remeasured, showed no crystal damage.

The structure was solved using heavy-atom and Fourier synthesis techniques and refined by full-matrix least-squares procedures.

All H atoms were located from a difference electron density map. The final least-squares refinement of atomic parameters with anisotropic thermal factors for the non-hydrogen atoms and isotropic thermal factors for the H atoms included a correction for isotropic extinction [refined G coefficient was 1·8 (0·1) × 10^{-6}] and converged to R = 0·044 for the observed reflexions. The weighting scheme $w = (1 + |F_o| +$

0567-7408/80/102458-03$01.00