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Key indicators

Single-crystal X-ray study T = 120 KMean $\sigma(\text{C}-\text{C}) = 0.003 \text{ Å}$ Disorder in solvent or counterion R factor = 0.032 wR factor = 0.090 Data-to-parameter ratio = 15.1

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

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8-Methyl-5-oxo-5,6-dihydrodipyrido[1,2-a:3',2'-e]pyrimidin-11-ium chloride trihydrate 120 K

In the structure of the title salt, $C_{12}H_{10}N_3O^+\cdot Cl^-\cdot 3H_2O$, the only species which do not coincide with the mirror plane in the space group $P6_3/m$ are one complete water molecule, one H atom of another water molecule and two H atoms of the methyl group of the cation. Consequently, apart from the two H atoms of the methyl group, the cation is completely planar. The hydrogen bonding between the water molecules and, through Cl^- anions, to the cations, although extensive, can be modelled satisfactorily only by treating one H atom in each of the two types of water molecules as disordered.

Comment

The title compound, (I), is an example of a more elaborate, potentially biologically active, pyridine-containing compound of the type provided by 2-chloronicotinoyl chloride, (II), as precursor, undergoing cyclization with a dinucleophilic reagent, in this case 2-amino-4-methylpyridine, (III). The asymmetric unit in the structure of (I) is shown in Fig. 1. Bond lengths and bond angles within the cation of (I) are summarized in Table 1. Particularly notable are the C4a-C5 and C10a-N2 distances of 1.468 (2) and 1.429 (2) Å, respectively, and the bond angles N6-C5-C4a [114.00 (14)°] and C6a-N6-C5 $[126.04 (14)^{\circ}]$. The somewhat extreme variation in bond lengths and more especially bond angles suggests that the cation is not altogether an aromatic species. This is certainly true of the lactam ring defined by C4a/C5/N6/C6a/ N2/C10a. In the refinement of the structure of (I) described here, the only atoms which are not coincident with a mirror plane of the space group $P6_3/m$ are two H atoms of the methyl group, one H atom of the water molecule involving O2 and the entire water molecule involving O3. As a consequence the cation, with the exception of the methyl H atoms, is completely flat and the entire structure can be described in terms of well defined layers parallel to (001) at $z = \frac{1}{4}$ and $\frac{3}{4}$ such as that shown in Fig. 2. Adjacent layers are related to one another by the operation of crystallographic centres of symmetry. The layers are also connected to one another by hydrogen bonding as described later. A further consequence of the mirror symmetry is that both water molecules must be present in two distinct orientations which must be present in equal numbers resulting, therefore, in disorder. For the water molecule involving O2, H1W is ordered but H2W is distributed over two mirror-plane-related sites both of occupancy 0.5. The atom H3W is common to both orientations of the water molecule involving O3 and is accompanied by H4W in one orientation and H5W in the other. Thus, while the H3W site is fully occupied, H4W and H5W both have occupancies of 0.5. The disorder of the H atoms has serious implications for the disposition of the hydrogen bonds in which they are

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Figure 1

The asymmetric unit of (I), together with other H atoms to complete the molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds.



Figure 2

A layer of ions at $z = \frac{1}{4}$. Displacement ellipsoids are drawn at the 50% probability level and H atoms involved in hydrogen-bond formation (dashed lines) are shown as small spheres of arbitrary radii. Selected atoms are labelled. [Symmetry codes: (iii) 1 - y, x - y, z; (iv) y - x, 1 - x, z; (v) 1 + y - x, 1 - x, z; (vi) 1 - y, 1 + x - y, z.]

involved (Table 2). As shown in Fig. 3, the majority of the hydrogen bonds given in Table 2 interconnect the water molecules to form infinite tube-like columns propagated in the direction of c. These constitute spines of connectivity with branches at $z = \frac{1}{4}$ and $\frac{3}{4}$ to Cl1 atoms which, by means of the N6–H6···Cl1 hydrogen bonds, extend the linkage to the cations. The surface of the aqueous 'tube' comprises six chains of the form shown in Fig. 4 connected to one another by hydrogen bonds of the form O3–H3W···O3ⁱ [symmetry code (i) 1 + x - y, x, 1 - z]. Notable here is the polarity, in the example shown in Fig. 4 in the positive direction of z, of the donor to acceptor alignment of the hydrogen bonds involved in the propagation of the chain in the [001] direction. Fig. 4



Figure 3

Hydrogen-bonds (dashed lines) within a column of water molecules and the attached Cl^- anions in the structure of (I). The view is approximately down *c*, with *a* running left to right across the page. The H atoms shown have been chosen so as to provide an ordered arrangement. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Selected atoms are labelled. The unit cell outline has been omitted for clarity.

shows an arbitrary choice of mutually compatible H atoms consistent with only one of the two possible polarities of the chain. This ordered arrangement is clearly incompatible, as far as the H atoms are concerned, with the mirror planes upon which the O2 atoms lie and which relate the O3 atoms to one another. Clearly chains of this and of the opposite polarity must be distributed throughout the structure in equal numbers in order to bring about the observed disorder. Weak C– $H \cdots O$ contacts, also given in Table 2, provide, as shown in Fig. 2, inter-cation connectivity within the layers.



Experimental

To a solution of 2-chloronicotinoyl chloride, (II) (1.0 g, 5.68 mmol), in anhydrous tetrahydrofuran (30 ml) were successively added, with stirring, 2-amino-4-methylpyridine, (III) (1.1 ml, 5.68 mmol), and



Figure 4

A more detailed view, with an arbitrary choice of mutually compatible H atoms, of the hydrogen-bond connectivity between O2 and O3 along the length of a single chain within the column of Fig. 3. The *c* axis runs from left to right across the page. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Selected atoms are labelled. The unit cell outline has been omitted for clarity. [Symmetry codes: (ii) $x, y, \frac{3}{2} - z$; (vii) $x, y, \frac{1}{2} - z$; (viii) x, y, 1 + z.]

triethylamine (1.63 ml, 11.36 mmol) at room temperature. The reaction mixture was stirred for 8 h at room temperature, quenched with water (20 ml), and ethyl acetate (15 ml) was added. The organic layer was collected, washed with saturated sodium bicarbonate solution (2 × 20 ml), dried over sodium sulfate and rotary evaporated. The residue was purified by chromatography, with hexane–ethyl acetate (7:3) as eluant. The sample used in the crystallographic study was recrystallized from ethanol (m.p. 535–536 K). ¹H NMR [400.00 MHz (FIDRES ±0.15 Hz), DMSO-*d*₆]: δ 9.80 (1H, *d*, *J* = 7.3 Hz, H10), 9.15 (1H, *dd*, *J* = 2.0 and 4.8 Hz, H2), 8.80 (1H, *dd*, *J* = 2.0 and 8.0 Hz, H4), 8.03 (1H, *dd*, *J* = 4.8 and 8.0 Hz, H3), 7.71 (1H, *s*, H7), 7.64 (1H, *dd*, *J* = 2.0 and 7.2 Hz, H9), 2.65 (3H, *s*, CH₃). ¹³C NMR (100.0 MHz, DMSO-*d*₆): δ 159.4 (C5), 157.9 (C10), 154.3 (C2), 147.0 (C6a), 146.1 (C10*a*), 137.9 (C4), 129.9 (C9), 126.7 (C3), 120.7 (C4a), 116.7 (C8), 114.8 (C7), 21.8 (CH₃). IR (cm⁻¹, KBr disk): v_{max} 3080 (NH), 1712 (C=O).

Crystal data

$C_{12}H_{10}N_3O^+ \cdot Cl^- \cdot 3H_2O$	Mo $K\alpha$ radiation
$M_r = 301.73$	Cell parameters from 3270
Hexagonal, $P6_3/m$	reflections
a = 19.4419 (3) Å	$\theta = 2.9-27.5^{\circ}$
c = 6.5498 (1) Å	$\mu = 0.28 \text{ mm}^{-1}$
V = 2144.05 (6) Å ³	T = 120 (2) K
Z = 6	Block, colourless
$D_x = 1.402 \text{ Mg m}^{-3}$	0.24 \times 0.12 \times 0.10 mm
Data collection	
Bruker–Nonius KappaCCD	1783 independent reflections
diffractometer	1600 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\rm int} = 0.036$
Absorption correction: multi-scan	$\theta_{\rm max} = 27.5^{\circ}$
(SADABS; Sheldrick, 2003)	$h = -22 \rightarrow 25$
$T_{\min} = 0.649, \ T_{\max} = 1.000$	$k = -25 \rightarrow 25$
16137 measured reflections	$l = -8 \rightarrow 8$
Refinement	
\mathbf{D} (\mathbf{r}^2	$4/5^{2}(E^{2})$ (0.040(D) ²

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.090$ S = 1.151783 reflections 118 parameters H-atom parameters constrained $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0426P)^{2} + 0.6158P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$ $(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{max} = 0.25 \text{ e} \text{ Å}^{-3}$

$$\Delta \rho_{\rm min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Table	1
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Summary of geometric parameters (Å, $^{\circ}$) in the cation of (I).

Parameter ^a	Min.	Max. ^b	
$C_4 - C_3^{c}$	1.498 (2)		
$C_3 - C_3$	1.351 (2)	1.468 (2)	
$C_3 - N_3$	1.358 (2)	1.429 (2)	
$C_3 - N_2$	1.323 (2)	1.333 (2)	
$C_3 - O_1^d$	1.216 (2)		
$X - Y - Z^e$	114.00 (14)	126.04 (14)	

Notes: (a) bond type indicated by atoms with subscripts corresponding to the atom connectivities; (b) only present for multiple occurrences; (c) C11-C8; (d) C5-O1; (e) internal angles of the ring system.

°).

Fable 2		
Hydrogen-bond	geometry	(Å,

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
N6—H6···Cl1	0.88	2.23	3.0976 (15)	168
$O2 - H1W \cdot \cdot \cdot Cl1$	0.86	2.25	3.1061 (13)	172
$O2 - H2W \cdots O3$	0.82	1.94	2.7108 (13)	157
$O3 - H3W \cdots O3^{i}$	0.81	1.93	2.7263 (9)	172
$O3 - H4W \cdots O3^{ii}$	0.86	1.86	2.7042 (19)	165
$O3 - H5W \cdots O2$	0.85	1.86	2.7108 (13)	177
C4−H4···O1 ⁱⁱⁱ	0.95	2.50	3.179 (2)	128
$C9 - H9 \cdots O2^{iv}$	0.95	2.54	3.357 (2)	144
Summerstand and (i) a		1. (::)	3. (:::)	

Symmetry codes: (i) x - y + 1, x, -z + 1; (ii) $x, y, -z + \frac{3}{2}$; (iii) -y + 1, x - y, z; (iv) -x + y, -x + 1, z.

Initial positions for the H atoms of the water molecules were obtained from difference maps, revised to provide a realistic hydrogen-bonding scheme and the geometry of the water molecules idealized to provide O–H distances and H–O–H angles in the ranges 0.81–0.86 Å and 105–111°, respectively. All other H atoms were placed in calculated positions, with C–H distances set at 0.95 and 0.98 Å for aryl and methyl H atoms, respectively, and the N–H distance set to 0.88 Å for the H atom of the NH group, placed as for an aryl H atom. The H atoms of the methyl group, H11A and H11B, were placed in positions appropriate to the mirror plane site symmetry of the group whose orientation was therefore fixed accordingly. In all cases, the H atoms were then refined using a riding model, with $U_{iso}(H) = 1.3U_{eq}(C,N,O)$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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