

2-Amino-5-methylpyridinium (2-amino-5-methylpyridine)trichloro- zincate(II)

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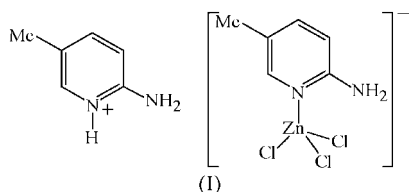
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The title compound, $(C_6H_9N_2)[ZnCl_3(C_6H_8N_2)]$, consists of one 2-amino-5-methylpyridinium cation and one (2-amino-5-methylpyridine)trichlorozincate(II) anion, which are held together by $N-H\cdots Cl$ hydrogen bonds and $\pi-\pi$ interactions. The cation and the pyridine ligand show similar geometric features, except for the $N-C$ bond lengths. Molecules of the title compound are connected by $N-H\cdots Cl$ hydrogen bonds to form chiral chains; these chains are associated further by $C-H\cdots Cl$ hydrogen bonds to form layers, which are in turn linked by $\pi-\pi$ interactions.

Comment

There are numerous examples of 2-amino-substituted pyridine compounds in which the 2-aminopyridines act as ligands (Ranninger *et al.*, 1985; Krizanovic *et al.*, 1993; Luque *et al.*, 1997; Qin *et al.*, 1999; Yip *et al.*, 1999; Lah *et al.*, 2002; Ren *et al.*, 2002; Rivas *et al.*, 2003) or as protonated cations (Luque *et al.*, 1997; Jin *et al.*, 2000, 2001, 2002, 2005; Albrecht *et al.*, 2003). All of these studies provide important references to further research into 2-aminopyridines. We have synthesized the title compound, (I), where 2-amino-5-methylpyridine (AMP) appears both as a ligand and as a protonated cation.



The title compound consists of one AMP cation (HAMP) and one AMP ligand (LAMP) coordinated with a $[ZnCl_3]^-$ anion. These two moieties are held together by $N2-H2A\cdots Cl3$ [3.301 (3) Å] and $N4-H4B\cdots Cl2$ [3.322 (3) Å]

hydrogen bonds, and by a $\pi-\pi$ interaction with a separation of 3.623 (3) Å between the centroids of the HAMP and LAMP moieties (Fig. 1 and Table 2). In the formula unit, the LAMP molecule lies almost perfectly parallel to the HAMP cation, as indicated by the dihedral angle of 0.6 (3)° between their planes. Atom Cl3 lies 0.708 (4) Å out of the LAMP ring plane, while atom Cl2 lies 1.089 (4) Å out of the HAMP ring plane.

In the HAMP cation, the $N4-C11$ bond [1.329 (4) Å] is shorter than the $N3-C11$ [1.342 (3) Å] and $N3-C7$ [1.349 (4) Å] bonds, and the $C10-C11$ [1.398 (4) Å] and $C8-C9$ [1.399 (4) Å] bonds are significantly longer than the $C9-C10$ [1.351 (4) Å] and $C7-C8$ [1.347 (4) Å] bonds. In the LAMP molecule, all the $C-N$ bonds are comparable to one another, and the $C-C$ bond-length features are similar to those in the HAMP cation (Table 1). In contrast, in the solid-state structure of AMP (Nahringbauer & Kvik, 1977), the $N-C$ bond out of the ring is clearly longer than that in the

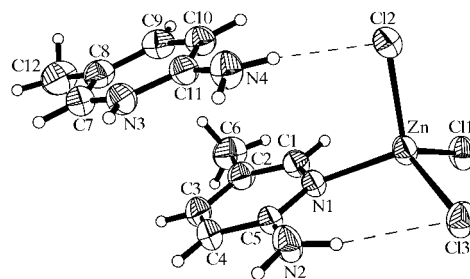


Figure 1

The cell unit of (I), with the atom labelling, showing 40% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed lines.

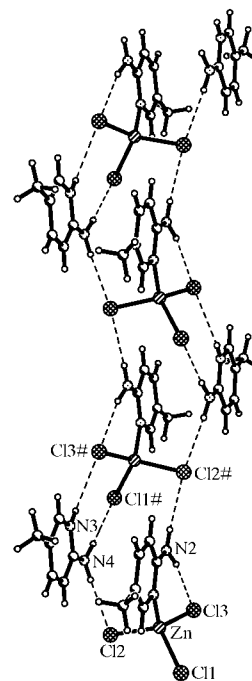


Figure 2

The chiral hydrogen-bonded chain of (I) along the [010] direction. Hydrogen bonds are indicated by dashed lines. Atoms labeled with a hash (#) are at the symmetry position $(-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2})$.

ring, and the C—C bond-length differences are less pronounced. The geometric features of the HAMP cation resemble those observed in other 2-aminopyridine structures (Luque *et al.*, 1997; Jin *et al.*, 2000, 2001, 2002, 2005; Albrecht *et al.*, 2003) that are believed to be involved in amine–imine tautomerism (Inuzuka & Fujimoto, 1986, 1990; Ishikawa *et al.*, 2002). The geometric features of the LAMP molecule are similar to those of some other coordinated 2-aminopyridines (Ranninger *et al.*, 1985; Krizanovic *et al.*, 1993; Qin *et al.*, 1999; Yip *et al.*, 1999; Lah *et al.*, 2002; Ren *et al.*, 2002). The reason for the deviations of the LAMP geometry from that of a normal AMP molecule remains unknown.

Molecules of (I) are connected to form a one-dimensional chiral chain along the [010] direction via N3—H3N⁺···Cl3⁻, N2—H2B⁺···Cl2⁻ and N4—H4A⁺···Cl1⁻ hydrogen bonds (Fig. 2; symmetry code as in Table 2). Between two adjacent molecules of (I) in the chain, three hydrogen-bonded rings, *viz.* R₄ⁱ(12), R₂ⁱⁱ(8) and R₁ⁱⁱⁱ(6) [using the notation of Etter (1990) and Grell *et al.* (2000)], are embedded in a larger R₃^{iv}(14) hydrogen-bonded ring (Fig. 2). Two neighboring chains, which are inversely related, are associated by a C9—H9···Cl1ⁱⁱ contact (Table 2), and therefore the chirality is countervailed. A layer parallel to (101) is established by translation of the two inversely related chains. Finally, the whole structure is established by translation of the layer. There are π–π interactions (Sharma *et al.*, 1993; Pedireddi *et al.*, 1996) between neighboring layers, with a centroid-to-centroid distance of 3.908 (4) Å between the LAMP and HAMP moieties. A C12—H12B···π contact (LAMP; symmetry code: $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$) [with a distance of 3.325 (3) Å between the H atom and the

centroid of the LAMP molecule] plays a subordinate role in stabilizing the structure.

Experimental

2-Amino-5-methylpyridine, ZnCl₂ and aqueous HCl in a 2:1:1 molar ratio were mixed and dissolved in sufficient ethanol by heating to a temperature at which a clear solution resulted. Crystals of (I) were formed by gradual evaporation of the ethanol over a period of one week at 303 K, producing a final yield of 56% based on AMP. IR (KBr, cm⁻¹): 3415 (s), 3333 (s), 3284 (s), 3200 (s), 3081, 3053, 2924, 1670 (s), 1645 (s), 1617 (s), 1569, 1555, 1515 (s), 1463, 1406, 1347, 1329, 1279, 1239, 1210, 1154, 1091, 1041, 832, 777, 717, 667, 648, 510, 460, 437.

Crystal data

(C₆H₉N₂)[ZnCl₃(C₆H₈N₂)]
M_r = 389.02
 Monoclinic, *P*₂₁/*n*
a = 9.254 (3) Å
b = 13.726 (4) Å
c = 13.572 (5) Å
 β = 102.57 (3)°
V = 1682.6 (10) Å³
Z = 4

D_x = 1.536 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3253 reflections
 θ = 2.4–26.0°
 μ = 1.93 mm⁻¹
T = 293 (2) K
 Prism, colorless
 0.30 × 0.25 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.57, *T_{max}* = 0.65
 8903 measured reflections

3304 independent reflections
 2518 reflections with *I* > 2σ(*I*)
R_{int} = 0.049
 θ_{max} = 26.0°
h = -11 → 10
k = -15 → 16
l = -14 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.072
S = 0.93
 3304 reflections
 203 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.25 \text{ e \AA}^{-3}$

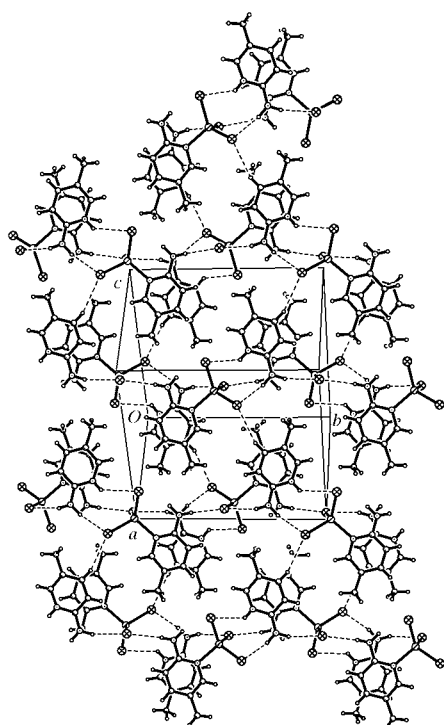


Figure 3 The layer formation in the structure of (I), parallel to (101). Hydrogen bonds are indicated by dashed lines.

Table 1 Selected interatomic distances (Å).

Zn—N1	2.037 (2)	C5—N1	1.342 (3)
Zn—Cl1	2.2558 (9)	C5—N2	1.347 (4)
Zn—Cl3	2.2597 (11)	C7—C8	1.347 (4)
Zn—Cl2	2.2617 (12)	C7—N3	1.349 (4)
Cl1—N1	1.351 (3)	C8—C9	1.399 (4)
Cl1—C2	1.364 (4)	C8—C12	1.504 (4)
C2—C3	1.394 (4)	C9—C10	1.351 (4)
C2—C6	1.498 (4)	C10—C11	1.398 (4)
C3—C4	1.352 (4)	C11—N4	1.329 (4)
C4—C5	1.401 (4)	C11—N3	1.342 (3)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2A···Cl3	0.96 (2)	2.38 (2)	3.301 (3)	162 (2)
N2—H2B···Cl2 ⁱ	0.87 (2)	2.47 (2)	3.335 (3)	174 (3)
N3—H3N···Cl3 ⁱ	0.86 (2)	2.65 (2)	3.279 (3)	131 (2)
N4—H4B···Cl2	0.91 (2)	2.45 (2)	3.322 (3)	162 (3)
N4—H4A···Cl1 ⁱ	0.96 (2)	2.37 (2)	3.315 (3)	168 (3)
C9—H9···Cl1 ⁱⁱ	0.93	2.88	3.770 (3)	162

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

H atoms attaching to N atoms were located in difference Fourier maps and their parameters were refined freely. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C–H distances of 0.93 (aromatic) and 0.96 Å (methyl), and $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times the U_{eq} values of the parent atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1045). Services for accessing these data are described at the back of the journal.

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