Bis(2-amino-6-methylpyridinium) tetrachlorozincate(II)

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The title compound, $(C_6H_9N_2)_2[Zn^{II}Cl_4]$, consists of two 2-amino-6-methylpyridinium (AMP) cations and one $[ZnCl_4]^{2-}$ anion, which are held together by $N-H\cdots Cl$ hydrogen bonds. Bond lengths within the AMP cation indicate that the imine tautomer makes a significant contribution to the structure. The molecules are associated by two different $\pi-\pi$ interactions between identical antiparallel AMP cations, with face-to-face distances of 3.627 (4) and 3.342 (3) Å, to form a one-dimensional chain.

Comment

Protonated 2-aminopyridine always undergoes aminium–iminium tautomerism (see first scheme below) (Inuzuka & Fujimoto, 1986, 1990; Ishikawa *et al.*, 2002).
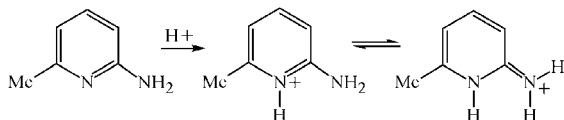
Previously, the tautomerism has been evidenced by X-ray diffraction in some 2-amino-*X*-methylpyridine adducts (2A*X*MP; *X* indicates the methyl position), such as 2A3MP–maleic acid (2/3) (Jin *et al.*, 2002), 2A6MP–neoabietic acid (1/1) (Jin *et al.*, 2000) and 2A3MP–phthalic acid (2/1) (Jin *et al.*, 2001). As a continuation of our research, the title compound, (I), has been synthesized. The structure is discussed here.
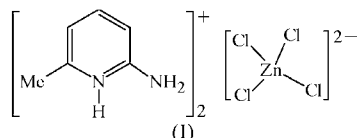
There are two crystallographically independent 2-amino-6-methylpyridinium (AMP) cations and a $[ZnCl_4]^{2-}$ anion in the

formula unit (Fig. 1). The $[ZnCl_4]^{2-}$ anion is linked to cation AMP(*A*) (N1/N2/C1–C6) by $N1-H1\cdots Cl2$ and $N2-H21\cdots Cl2$ hydrogen bonds, and to cation AMP(*B*) (N3/N4/C7–C12) by $N3-HN\cdots Cl4$ and $N4-H41\cdots Cl4$ hydrogen bonds (Fig. 1 and Table 2). The hydrogen-bonded rings shown in Fig. 1 could be described by the graph-set motif $R_2^1(6)$ (Etter, 1990; Grell *et al.*, 2000). Atom Cl4 is perfectly coplanar with the AMP(*B*) ring, with a deviation of 0.007 (5) Å from the mean plane, whereas atom Cl2 lies 0.337 (5) Å from the plane of the AMP(*A*) ring. In the formula unit, the dihedral angle between the planes of the two AMP cations is 95.53 (8)°.

The geometric features of both ammonium and iminium tautomers are obvious in a compound in which coordinated and protonated 2-aminopyridine co-exist (Luque *et al.*, 1997). In contrast, features of the iminium tautomer are most clearly observed in (I), suggesting that the imime tautomer makes a greater contribution to the structure. In cation AMP(*A*), the $N2-C1$ bond [1.326 (4) Å] is slightly but significantly shorter
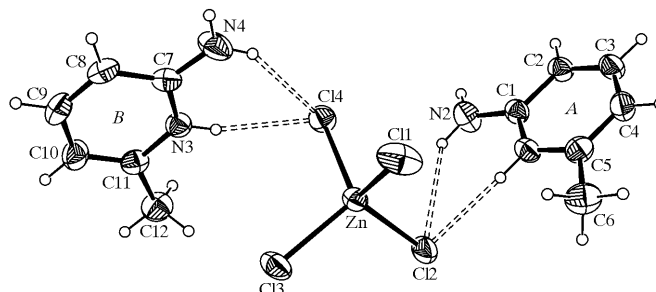
Figure 1
The AMP and $[ZnCl_4]^{2-}$ units in the title salt, shown with the atom labelling. Displacement ellipsoids are shown at the 30% probability level and hydrogen bonds are illustrated as dashed lines.
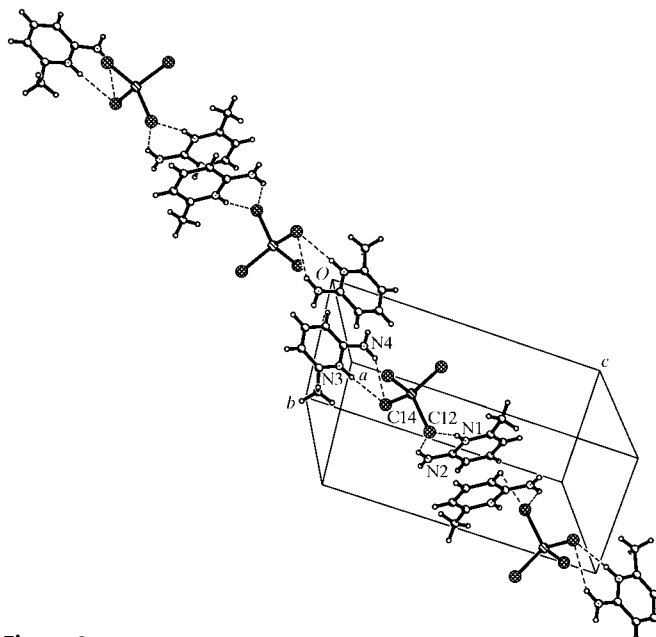
Figure 2
Part of the crystal structure of the title salt, showing the infinite chain of $\pi-\pi$ interactions along the [111] direction. Hydrogen bonds are indicated by dashed lines.

than the N1—C1 [1.351 (4) Å] and N1—C5 [1.359 (4) Å] bonds, consistent with the iminium tautomer (Table 1). Moreover, the existence of the iminium tautomer is supported by the fact that the C1—C2 [1.403 (4) Å] and C3—C4 [1.387 (4) Å] bonds are longer than the C2—C3 [1.347 (4) Å] and C4—C5 [1.357 (4) Å] bonds. Similar features are also observed in cation AMP(*B*).

Generally, the Zn—Cl bond lengths and Cl—Zn—Cl bond angles in a $[ZnCl_4]^{2-}$ anion are not equal to one another (Ferbinteanu *et al.*, 1998; Kubicki & Szafranski, 1998; Wick-leder, 2001; Albrecht *et al.*, 2003) but vary with the environment around the Cl atoms. In (I), as atoms Cl2 and Cl4 are involved in stronger and more numerous N—H···Cl hydrogen bonds than atoms Cl1 and Cl3, the Zn—Cl2 and Zn—Cl4 bonds are obviously longer than the Zn—Cl1 and Zn—Cl3 bonds. The mean value of the Zn—Cl bond lengths is 2.2579 (9) Å. The Cl—Zn—Cl angles range from 106.87 (4) to 112.37 (4)°. Owing to the obvious differences of the Zn—Cl distances and the Cl—Zn—Cl angles, the coordination geometry of the Zn atom could be regarded as a distorted tetrahedron.

It is expected that two AMP cations will repel each other owing to the electrostatic force between positive charges. However, in the solid state of (I), there are antiparallel pairs of cations AMP(*A*) with AMP(*A*) at $(1 - x, 1 - y, 1 - z)$, as well as pairs of cations AMP(*B*) with AMP(*B*) at $(1 - x, -y, -z)$, these pairs being governed by π–π interactions (Sharma *et al.*, 1993; Pedireddi *et al.*, 1996) with face-to-face distances of 3.627 (4) and 3.748 (3) Å, respectively. The π–π interactions can be interpreted as the electrostatic attraction between unevenly distributed charge across the π system of the anti-parallel AMP cations (Muehldorf *et al.*, 1988).

As shown in Fig. 2, (I) is connected by π–π interactions between antiparallel pairs of AMP cations to form a one-dimensional chain along the [111] direction. Neighboring chains are associated with one another principally by N2—H22···Cl1[i] and N4—H42···Cl3[ii] hydrogen bonding and are interrelated by translation, thus resulting in the building up of the whole crystal structure. In general, the structure is characterized by organic and inorganic layers (Fig. 3). There is a C6—H6*B*···Cl1 hydrogen bond (Braga *et al.*, 1999; Janiak & Scharmann, 2003) which plays a subordinative role in stabilizing the structure (Table 2).

Experimental

Crystal data

$(C_6H_9N_2)_2[ZnCl_4]$	$Z = 2$
$M_r = 425.49$	$D_x = 1.531$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.6642$ (8) Å	Cell parameters from 39
$b = 7.9235$ (8) Å	reflections
$c = 15.6651$ (16) Å	$\theta = 2.8$–14.9°
$\alpha = 81.177$ (2)°	$\mu = 1.91$ mm^{-1}
$\beta = 79.128$ (2)°	$T = 273$ (2) K
$\gamma = 89.983$ (2)°	Block, colorless
$V = 922.77$ (16) Å^3	$0.37 \times 0.19 \times 0.14$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3335 independent reflections
	2791 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.012$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$\theta_{max} = 25.2°$
	$h = -9 \rightarrow 8$
$T_{min} = 0.654$, $T_{max} = 0.776$	$k = -9 \rightarrow 9$
4948 measured reflections	$l = -14 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 0.1635P]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3272 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
192 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

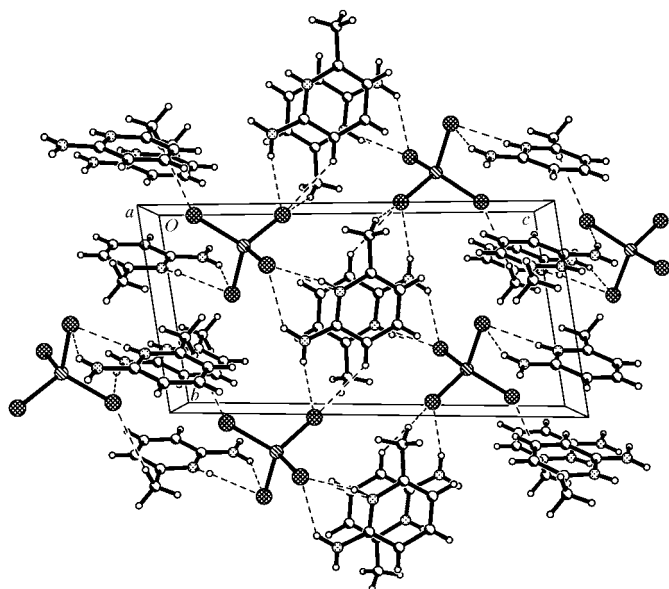|			
Cl1—Zn	2.2358 (9)	C4—C5	1.357 (4)
Cl2—Zn	2.2767 (8)	C5—C6	1.496 (4)
Cl3—Zn	2.2396 (8)	N3—C7	1.350 (4)
Cl4—Zn	2.2786 (8)	N3—C11	1.365 (4)
N1—C1	1.351 (4)	N4—C7	1.329 (4)
N1—C5	1.359 (4)	C7—C8	1.394 (4)
N2—C1	1.326 (4)	C8—C9	1.354 (5)
C1—C2	1.403 (4)	C9—C10	1.389 (5)
C2—C3	1.347 (4)	C10—C11	1.348 (4)
C3—C4	1.387 (4)	C11—C12	1.495 (4)
Cl1—Zn—Cl3	112.41 (4)	Cl1—Zn—Cl4	107.17 (3)
Cl1—Zn—Cl2	111.75 (4)	Cl3—Zn—Cl4	110.74 (4)
Cl3—Zn—Cl2	107.77 (3)	Cl2—Zn—Cl4	106.88 (3)

Figure 3
A packing diagram for the title salt, viewed along the *a* axis. Hydrogen bonds are indicated by dashed lines.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$Cl2	0.86	2.31	3.155 (2)	167
N2—H21$\cdots$Cl2	0.86	2.83	3.555 (3)	143
N2—H22$\cdots$Cl1^i	0.86	2.51	3.331 (3)	160
N3—H3$\cdots$Cl4	0.86	2.38	3.218 (2)	164
N4—H41$\cdots$Cl4	0.86	2.69	3.448 (3)	148
N4—H42$\cdots$Cl3^{ii}	0.86	2.54	3.378 (3)	165
N4—H42$\cdots$Cl2^{ii}	0.86	2.96	3.382 (3)	112
C2—H2$\cdots$Cl1^i	0.93	2.89	3.651 (3)	140
C6—H6$B\cdots$Cl1^{iii}	0.96	3.28	3.713 (4)	110
C12—H12$B\cdots$Cl3	0.96	2.98	3.851 (4)	151
C8—H8$\cdots$Cl3^{iv}	0.93	2.97	3.632 (3)	129

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

All H atoms could be found in difference Fourier maps, but were introduced in calculated positions and allowed to ride on their parent atoms at distances of 0.86 (N—H), 0.93 (C—H aromatic) and 0.96 Å (methyl), with U_{iso}(H) values of 1.2–1.5 times U_{eq} 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: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1068). Services for accessing these data are described at the back of the journal.

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