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Bis(2-aminopyridinium) tetrachloridozincate(II)

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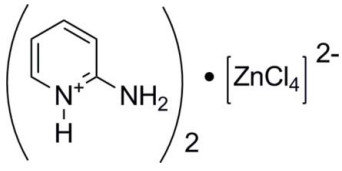
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.103; data-to-parameter ratio = 18.9.

In the title compound, $(C_5H_7N_2)_2[ZnCl_4]$, the pyridine N atoms are protonated and the $[ZnCl_4]^{2-}$ anions adopt a slightly distorted tetrahedral configuration. In the crystal, weak N—H···Cl hydrogen bonds link the molecules into layers, while weak π–π interactions [centroid–centroid distance = 4.2758 (18) Å] also help to stabilize the packing.

Related literature

For background to phase transition materials, see: Li *et al.* (2008); Ye *et al.* (2009); Zhang *et al.* (2010)



Experimental

Crystal data

$(C_5H_7N_2)_2[ZnCl_4]$
M_r = 397.42
Monoclinic, $C2/c$
a = 8.3520 (17) Å
b = 14.198 (3) Å
c = 13.913 (3) Å
β = 93.70 (3)°
V = 1646.5 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.13 mm^{-1}
T = 298 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.653, T_{max} = 0.659
8175 measured reflections
1870 independent reflections
1612 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.21
1870 reflections
99 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl1	0.90 (4)	2.44 (4)	3.335 (3)	170 (3)
N1—H1A···Cl2^{i}	0.88 (4)	2.42 (4)	3.291 (3)	168 (4)
N2—H2A···Cl1^{ii}	0.87 (3)	2.61 (3)	3.325 (2)	140 (3)

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2229).

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Zhang, W., Ye, H. Y., Cai, H. L., Ge, J. Z., Xiong, R. G. & Huang, S. D. (2010). *J. Am. Chem. Soc.* **131**, 7300–7302.

supporting information

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S1. Comment

The asymmetric unit of the title compound is built up from one protonated 2-amino-pyridinium cation where the non-hydrogen atoms are practically co-planar with a mean deviation of 0.0101 (3)Å and a half of $[ZnCl_4]^{2-}$ anion (Fig. 1). The $[ZnCl_4]^{2-}$ anion is slightly distorted with the Zn—Cl distances and Cl—Zn—Cl angles of 2.2800 (8)Å to 2.2819 (8)Å and 104.40 (3)° to 114.65 (4)°, respectively. In the crystal structure (Fig. 2), π-π packing interactions of adjacent pyridine rings with a *Cg*1—*Cg*2 distance of 4.2758 (18)Å link the cations chains along *b* axis. The N—H···Cl hydrogen bonds with the average N—Cl distances of 3.317 A link the cations and anions into plan parallel to [1 1 0].

S2. Experimental

As a continuation of our study of phase transition materials (Li *et al.*, 2008, Ye *et al.*, 2009, Zhang *et al.*, 2010,), we performed dielectric studies (capacitance and dielectric loss measurements) using an automatic impedance TongHui2828 Analyzer on samples that were pressed into tablets on the surfaces of which a conducting carbon glue was deposited. Unfortunately, there was no distinct anomaly observed from 93 K to 420 K, (m.p. 438–440 K), suggesting that this compound should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range.

1.36 g (10 mmol)$ZnCl_2$ was firstly dissolved in 20 ml 1*M* HCl solution, to which 0.94 g (10 mmol) 2-amino-pyridine ethanol solution was then added under stirring. Ethanol was added until the precipitated substrates disappeared, then the solution was allowed to slowly evaporate at room temperature until prisms of the title were grown.

S3. Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with U_{iso}(H) = 1.2U_{eq}(C). The other H atoms bonded to N atom were found in the difference maps and refined freely.

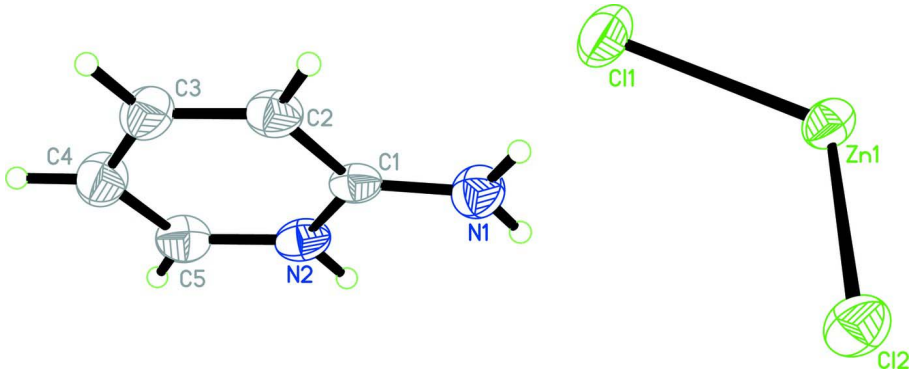

Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

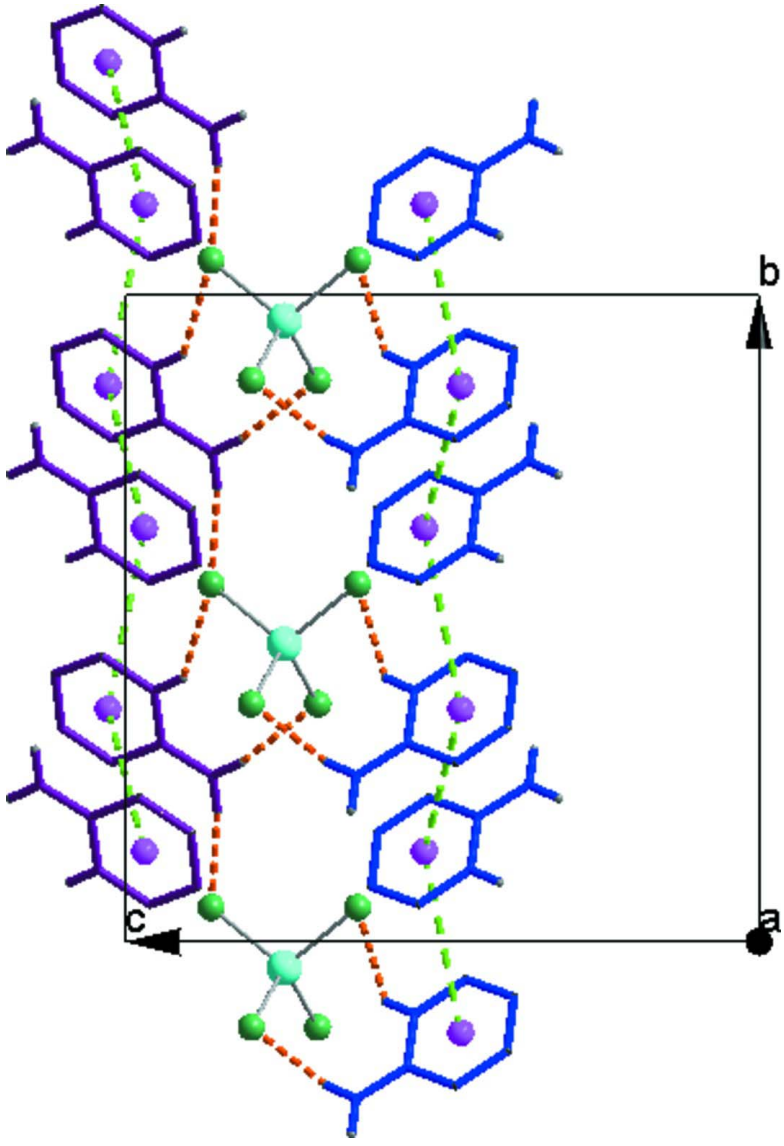

Figure 2

A view of the packing of the title compound, stacking along the *a* axis. Dashed lines indicate hydrogen bonds and π-π packing interactions.

Bis(2-aminopyridinium) tetrachloridozincate(II)

Crystal data

$(C_5H_7N_2)_2[ZnCl_4]$
$M_r = 397.42$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 8.3520\ (17)$ Å
$b = 14.198\ (3)$ Å
$c = 13.913\ (3)$ Å
$\beta = 93.70\ (3)°$
$V = 1646.5\ (6)$ Å^3
$Z = 4$
$F(000) = 800$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3679 reflections
$\theta = 3.1–27.4°$
$\mu = 2.13$ mm^{-1}
$T = 298$ K
Prism, colourless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.653, T_{max} = 0.659
8175 measured reflections
1870 independent reflections
1612 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.4°, θ_{min} = 3.1°
h = −10→10
k = −18→18
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.21
1870 reflections
99 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.9383P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.5000	0.53941 (3)	0.2500	0.04169 (16)
Cl1	0.40003 (10)	0.44657 (6)	0.36567 (7)	0.0650 (3)
Cl2	0.71122 (9)	0.63194 (5)	0.30264 (6)	0.0577 (2)
N1	0.5979 (3)	0.2427 (2)	0.3635 (2)	0.0569 (6)
H1B	0.543 (4)	0.297 (3)	0.356 (3)	0.071 (11)*
H1A	0.655 (5)	0.222 (3)	0.317 (3)	0.083 (12)*
N2	0.6702 (3)	0.11162 (17)	0.45575 (19)	0.0495 (6)
H2A	0.728 (4)	0.092 (2)	0.410 (2)	0.055 (9)*
C1	0.5877 (3)	0.19378 (19)	0.44405 (19)	0.0432 (6)
C2	0.4952 (3)	0.2225 (2)	0.5209 (2)	0.0510 (6)
H2B	0.4328	0.2793	0.5154	0.061*
C3	0.4951 (4)	0.1691 (2)	0.6022 (2)	0.0586 (7)
H3A	0.4330	0.1893	0.6541	0.070*
C4	0.5850 (4)	0.0851 (2)	0.6126 (2)	0.0606 (8)
H4A	0.5839	0.0479	0.6702	0.073*

C5	0.6707 (4)	0.0582 (2)	0.5376 (2)	0.0556 (7)
H5A	0.7304	0.0028	0.5419	0.067*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0398 (2)	0.0381 (2)	0.0484 (3)	0.000	0.01243 (18)	0.000
Cl1	0.0636 (5)	0.0588 (4)	0.0761 (5)	0.0085 (3)	0.0311 (4)	0.0244 (4)
Cl2	0.0556 (4)	0.0519 (4)	0.0656 (5)	−0.0148 (3)	0.0046 (3)	−0.0023 (3)
N1	0.0571 (15)	0.0612 (16)	0.0533 (14)	0.0015 (13)	0.0096 (12)	−0.0039 (12)
N2	0.0394 (11)	0.0509 (13)	0.0591 (14)	−0.0010 (10)	0.0097 (10)	−0.0149 (11)
C1	0.0322 (11)	0.0480 (14)	0.0494 (15)	−0.0047 (10)	0.0016 (10)	−0.0103 (11)
C2	0.0431 (13)	0.0548 (16)	0.0554 (16)	0.0072 (12)	0.0050 (12)	−0.0104 (13)
C3	0.0556 (17)	0.0704 (19)	0.0509 (17)	0.0036 (14)	0.0127 (13)	−0.0078 (14)
C4	0.0625 (18)	0.0605 (18)	0.0595 (18)	−0.0003 (15)	0.0077 (14)	0.0036 (14)
C5	0.0500 (16)	0.0469 (14)	0.070 (2)	0.0017 (12)	0.0029 (14)	−0.0020 (13)

Geometric parameters (Å, º)

Zn1—Cl1	2.2800 (8)	N2—H2A	0.87 (3)
Zn1—Cl1^{i}	2.2800 (8)	C1—C2	1.419 (4)
Zn1—Cl2	2.2819 (8)	C2—C3	1.362 (4)
Zn1—Cl2^{i}	2.2819 (8)	C2—H2B	0.9601
N1—C1	1.326 (4)	C3—C4	1.412 (5)
N1—H1B	0.90 (4)	C3—H3A	0.9599
N1—H1A	0.88 (4)	C4—C5	1.359 (4)
N2—C1	1.359 (4)	C4—H4A	0.9600
N2—C5	1.368 (4)	C5—H5A	0.9300
Cl1—Zn1—Cl1^{i}	109.36 (5)	N2—C1—C2	116.9 (3)
Cl1—Zn1—Cl2	114.65 (4)	C3—C2—C1	119.7 (3)
Cl1^{i}—Zn1—Cl2	104.40 (3)	C3—C2—H2B	120.2
Cl1—Zn1—Cl2^{i}	104.40 (3)	C1—C2—H2B	120.1
Cl1^{i}—Zn1—Cl2^{i}	114.65 (4)	C2—C3—C4	121.8 (3)
Cl2—Zn1—Cl2^{i}	109.70 (5)	C2—C3—H3A	119.2
C1—N1—H1B	120 (2)	C4—C3—H3A	119.0
C1—N1—H1A	121 (3)	C5—C4—C3	117.5 (3)
H1B—N1—H1A	120 (3)	C5—C4—H4A	121.3
C1—N2—C5	123.4 (2)	C3—C4—H4A	121.1
C1—N2—H2A	119 (2)	C4—C5—N2	120.6 (3)
C5—N2—H2A	117 (2)	C4—C5—H5A	119.7
N1—C1—N2	119.4 (3)	N2—C5—H5A	119.7
N1—C1—C2	123.6 (3)		
C5—N2—C1—N1	177.9 (3)	C1—C2—C3—C4	0.0 (5)
C5—N2—C1—C2	−1.7 (4)	C2—C3—C4—C5	−1.0 (5)

N1—C1—C2—C3	−178.2 (3)	C3—C4—C5—N2	0.7 (5)
N2—C1—C2—C3	1.3 (4)	C1—N2—C5—C4	0.7 (4)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···Cl1	0.90 (4)	2.44 (4)	3.335 (3)	170 (3)
N1—H1*A*···Cl2^{ii}	0.88 (4)	2.42 (4)	3.291 (3)	168 (4)
N2—H2*A*···Cl1^{iii}	0.87 (3)	2.61 (3)	3.325 (2)	140 (3)

Symmetry codes: (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) *x*+1/2, *y*−1/2, *z*.