Monoclinic
$P2_1/n$
$a$ = 11.087 (5) Å
$b$ = 10.4329 (10) Å
$c$ = 14.325 (9) Å
$\beta$ = 104.32 (2)°
$V$ = 1605.4 (13) Å$^3$
$Z$ = 2
$D_x$ = 1.576 Mg m$^{-3}$
$D_m$ not measured

Cell parameters from 25 reflections
$\theta$ = 14–22°
$\mu$ = 0.646 mm$^{-1}$
$T$ = 293 (2) K
Parallelepiped
0.6 × 0.4 × 0.1 mm
Black

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.822, $T_{max}$ = 0.937
4029 measured reflections
3840 independent reflections

2751 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.015
$\theta_{max}$ = 27.91°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 13$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.110
$S$ = 1.019
3840 reflections
203 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.032

$\Delta\rho_{max}$ = 0.486 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.288 e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0022 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (1b)*

| | | | |
|---|---|---|---|
| S1—C2 | 1.689 (2) | S3—C6 | 1.788 (3) |
| S1—C3 | 1.714 (2) | C1—C2 | 1.447 (3) |
| S2—C2 | 1.695 (2) | C1—C7 | 1.496 (3) |
| S2—C4 | 1.696 (3) | C3—C4 | 1.366 (3) |
| S3—C3 | 1.735 (2) | C4—C5 | 1.497 (3) |
| C2—S1—C3 | 96.50 (12) | C4—C3—S1 | 116.4 (2) |
| C2—S2—C4 | 97.66 (12) | C4—C3—S3 | 122.3 (2) |
| C3—S3—C6 | 101.94 (13) | S1—C3—S3 | 121.30 (14) |
| C2—C1—C7 | 115.2 (2) | C3—C4—C5 | 125.1 (2) |
| C1—C2—S1 | 127.9 (2) | C3—C4—S2 | 115.0 (2) |
| C1—C2—S2 | 117.6 (2) | C5—C4—S2 | 119.9 (2) |
| S1—C2—S2 | 114.40 (14) | | |

In (1*a*), the highest and deepest residual Fourier difference peaks were located 0.93 Å from I1.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1043). Services for accessing these data are described at the back of the journal.

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# 2-Amino-3,5-dichloropyridinium Chloride Monohydrate


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## Abstract

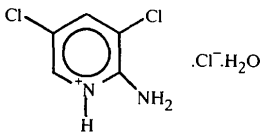
The monohydrate hydrochloride salt of 2-amino-3,5-dichloropyridine, $C_5H_5Cl_2N_2^+.Cl^-.H_2O$, was isolated from water by slow evaporation. The complex exhibits hydrogen bonds between the halide ions and both the pyridinium [3.109 (2) Å] and amino [3.303 (2) Å] protons. Bond lengths and angles are comparable to those of previously studied pyridine complexes. The C—Cl bond lengths are 1.732 (2) and 1.721 (2) Å, and the C—$NH_2$ bond length is 1.328 (2) Å.


## Comment

Our interest in low-dimensional magnetic lattices has resulted in the synthesis and study of a family of compounds with the formula $(LH)_2MX_4$, where $M$ is a transition metal in the 2+ state, $X$ is a halide, Cl or Br, and $LH$ is a protonated organic base. These compounds may pack in a crystal lattice in such a way that low-dimensional magnetic lattices are obtained. The magnetic lattice arises from interactions between the $MX_4^{2-}$ ions. The nature of these interactions is controlled by the crystal lattice, which changes as the organic base is changed. Compounds containing a base with a substituent in the 5 position, such

as 2-amino-5-methylpyridine (Place & Willet, 1987), 2-amino-5-chloropyridine (Albrecht *et al.*, 1997, 1998; Hammar *et al.*, 1997) and 2-amino-5-bromopyridinium (Román *et al.*, 1997), have shown interesting magnetic properties, whereas compounds with a substituent in the 3 position, such as 2-amino-3-methylpyridine (Coffey *et al.*, 1996), have been found to be unsuitable for generating magnetically useful lattices.

The title compound, (I), was synthesized to compare its suitability as a base with the previously mentioned derivatives and to determine whether substituents in the 3 position are detrimental to formation of the desired magnetic lattices. 2-Amino-3,5-dichloropyridinium chloride crystallizes as the monohydrate in space group $P2_1/c$.




(I)

The title compound (Fig. 1) is undistorted in the crystal lattice. Bond lengths and angles within the ring are normal (±0.02 Å and ±1.5°) when compared with those of other pyridinium compounds (Place & Willet, 1987; Coffey *et al.*, 1996; Kvick *et al.*, 1976). Hydrogen bonds form from the pyridinium proton to the Cl1 chloride ion; N1—H1···Cl1 3.109 (2) Å and 161°. The amino H atoms also form weak hydrogen bonds to Cl1; N2—H2*B*···Cl1 3.303 (2) Å and 150°. The water molecules are linked *via* hydrogen bonds both to the amino groups [O1···H2*A*—N2 2.856 (2) Å and 163°] and to the chloride ions [$Cl1^{i}$···H1O—O1 3.178 (2) Å and 170°; symmetry code: (i) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$]. Unlike 2-amino-5-chloropyridine (Kvick *et al.*, 1976), the title compound does not crystallize as dimers.

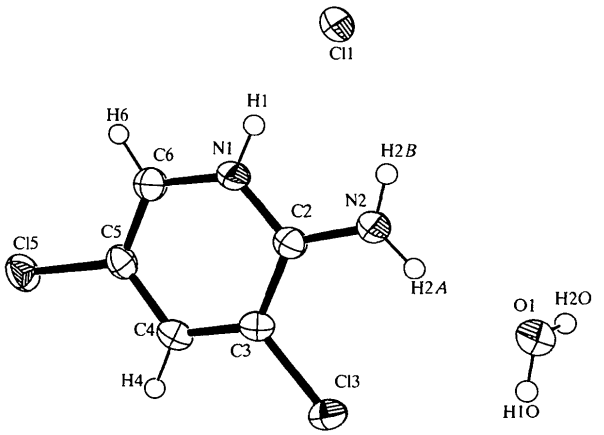



Fig. 1. The molecular structure of 2-amino-3,5-dichloropyridinium chloride monohydrate with 50% probability ellipsoids for non-H atoms.

The crystal lattice exists as pleated sheets that run roughly parallel to the *b* axis at an angle of −29.3° relative to the *a* axis (Fig. 2).

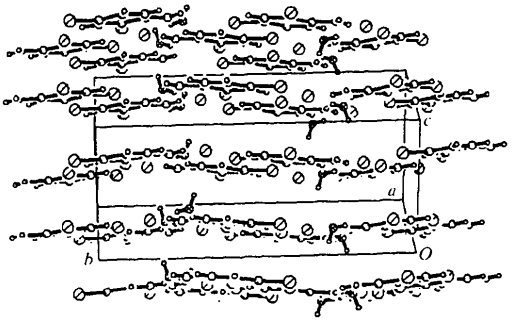



Fig. 2. View of the crystal packing.

The layers are linked by a hydrogen bond between the water molecule in one layer and a chloride ion in the next: $Cl1^{ii}$···H2O—O1 3.144 (2) Å and 177° [symmetry code: (ii) $x-1, y, z$]. Within the sheets, the pyridinium ions form zigzag chains parallel to the *ac* face and at an angle of −29.3° relative to the *a* axis. These chains are connected *via* hydrogen bonds to the chloride ions and water molecules.

The pyridinium rings do not stack in the same fashion as observed in complexes of 2-amino-5-chloropyridinium (Albrecht *et al.*, 1997, 1998) and 2-amino-3-methylpyridinium (Coffey *et al.*, 1996) salts. However, the rings do form a staggered stack parallel to the *c* axis and thus 2-amino-3,5-dichloropyridinium may still prove useful for generating the desired magnetic lattices. The synthesis of tetrahalo–metallate complexes is currently underway.

## Experimental

Crystals of 2-amino-3,5,-dichloropyridinium chloride monohydrate were grown by dissolving 2-amino-3,5-dichloropyridine in 1.0 *M* HCl and allowing slow evaporation of the solution. X-ray quality crystals were collected and air dried.

*Crystal data*

$C_5H_5Cl_2N_2^+.Cl^-.H_2O$
$M_r = 217.48$
Monoclinic
$P2_1/c$
$a = 6.7611\ (11)$ Å
$b = 16.889\ (3)$ Å
$c = 7.7713\ (13)$ Å
$\beta = 92.44\ (2)°$
$V = 886.6\ (3)$ Å$^3$
$Z = 4$
$D_x = 1.629$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 270 reflections
$\theta = 3.0$–$12.5°$
$\mu = 0.978$ mm$^{-1}$
$T = 153\ (2)$ K
Block
0.60 × 0.36 × 0.26 mm
Colorless

*Data collection*

Siemens *P*4 diffractometer
$\omega$ scans
Absorption correction:
$\psi$ scans (*SHELXTL*; Sheldrick, 1985)
$T_{min}$ = 0.687, $T_{max}$ = 0.775
4048 measured reflections
2029 independent reflections
1675 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025
$\theta_{max}$ = 27.48°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -10 \rightarrow 10$
3 standard reflections
every 97 reflections
intensity decay: 4.5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.071
$S$ = 0.958
2029 reflections
100 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl3—C3 | 1.721 (2) | C2—C3 | 1.419 (2) |
| Cl5—C5 | 1.732 (2) | C3—C4 | 1.357 (2) |
| N1—C2 | 1.342 (2) | C4—C5 | 1.401 (2) |
| N1—C6 | 1.357 (2) | C5—C6 | 1.349 (2) |
| N2—C2 | 1.328 (2) | | |
| C2—N1—C6 | 124.58 (15) | C2—C3—Cl3 | 117.77 (13) |
| N2—C2—N1 | 118.9 (2) | C3—C4—C5 | 119.2 (2) |
| N2—C2—C3 | 124.9 (2) | C6—C5—C4 | 120.3 (2) |
| N1—C2—C3 | 116.17 (15) | C6—C5—Cl5 | 119.88 (14) |
| C4—C3—C2 | 121.0 (2) | C4—C5—Cl5 | 119.84 (13) |
| C4—C3—Cl3 | 121.26 (13) | C5—C6—N1 | 118.8 (2) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···Cl1 | 0.85 | 2.29 | 3.109 (2) | 161 |
| N2—H2*B*···Cl1 | 0.82 | 2.57 | 3.303 (2) | 150 |
| N2—H2*A*···O1 | 0.86 | 2.02 | 2.856 (2) | 163 |
| O1—H1O···Cl1$^{i}$ | 0.82 | 2.37 | 3.178 (1) | 170 |
| O1—H2O···Cl1$^{ii}$ | 0.76 | 2.38 | 3.144 (2) | 172 |

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

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1985). 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: FR1087). Services for accessing these data are described at the back of the journal.

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# 2,3-Bis(diphenylmethylene)succinic Anhydride, (I), 2-(2-Adamantylidene)-3-(9-fluorenylidene)succinic Anhydride, (II), and 2-(9-Fluorenylidene)-3-(3,4,5-trimethoxybenzylidene)succinic Anhydride, (III)

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## Abstract

The title compounds are derivatives of dimethylenesuccinic anhydride and belong to the fulgide family of compounds. The fulgides were the first photochromic systems to be discovered. Fulgide (I) ($C_{30}H_{20}O_3$) possesses a crystallographic twofold axis. The divinylsuccinic anhydride moiety is not planar in fulgides (II) ($C_{27}H_{22}O_3$) and (III) ($C_{27}H_{20}O_6$). In both (II) and (III), the C atom bonded to the fluorenyl moiety deviates significantly from the mean plane through the five-membered ring of the fluorenyl moiety.


## Comment

Among the many classes of photochromic compounds, the fulgides, first discovered by Stobbe & Eckert (1905) and Stobbe (1911), are important for their relative stability (see the scheme below). Although the first com-

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