

Bis(4-chloropyridinium) tetrachlorido-nickelate(II)

Lili Cao,^a Ulli Englert^b and Qi Li^{a*}

^aCollege of Chemistry, Beijing Normal University, Xijiekouwai Street 19, Beijing 100875, People's Republic of China, and ^bInstitut für Anorganische Chemie, RWTH Aachen, Prof.-Pirlet-Strasse 1, 52074 Aachen, Germany

Correspondence e-mail: qili@bnu.edu.cn

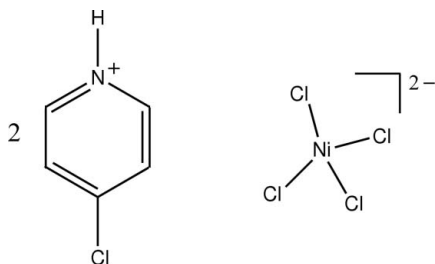
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.045; wR factor = 0.124; data-to-parameter ratio = 23.6.

In the title compound, $(\text{C}_5\text{H}_5\text{ClN})_2[\text{NiCl}_4]$, the dianion lies on a twofold rotation axis. Two cations are linked to each anion by classical $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds, and short $\text{Cl}\cdots\text{Cl}$ contacts and $\text{Cl}\cdots\pi$ stacking interactions [with distances of 3.376 (2) and 3.684 (2) Å, respectively] extend this pattern into a chain. The $[\text{NiCl}_4]^{2-}$ anion shows significant deviation from ideal tetrahedral geometry.

Related literature

For related literature, see: Espallargas *et al.* (2006); Luque *et al.* (2001); Willett *et al.* (2003).



Experimental

Crystal data

$(\text{C}_5\text{H}_5\text{ClN})_2[\text{NiCl}_4]$
 $M_r = 429.61$

Monoclinic, $C2/c$
 $a = 16.513$ (2) Å

$b = 7.2862$ (11) Å
 $c = 13.948$ (2) Å
 $\beta = 100.526$ (3)°
 $V = 1650.0$ (4) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.13$ mm⁻¹
 $T = 298$ (2) K
 $0.36 \times 0.28 \times 0.26$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.46$, $T_{\max} = 0.57$

5779 measured reflections
2049 independent reflections
1820 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.07$
2049 reflections

87 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.80$ e Å⁻³
 $\Delta\rho_{\min} = -0.98$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{Cl3}$	0.93	2.79	3.586 (4)	145
$\text{N1}-\text{H1}\cdots\text{Cl2}^i$	0.86	2.41	3.158 (3)	145
$\text{C5}-\text{H5A}\cdots\text{Cl2}^{ii}$	0.93	2.75	3.633 (4)	159

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2533).

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supplementary materials

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Comment

Short intermolecular $X\cdots X$ ($X = \text{F}, \text{Cl}, \text{Br}$) interactions in crystals have attracted increasing attention. The title compound is isotypic and probably isomorphous with $(4\text{-}X\text{pyH})_2[\text{Co}X_4]$, wherein $X' = \text{Cl}$, $X = \text{Cl}$ or $X' = \text{Br}$, $X = \text{Cl}$ (Espallargas *et al.*, 2006). Studies by Willett *et al.* have been devoted to bromopyridinium tetrahalocuprate salts (Willett *et al.*, 2003), and methyl pyridinium derivatives were reported earlier by Luque and his coworkers (Luque *et al.*, 2001). In the structure communicated here, the anionic building block is a $[\text{NiCl}_4]^{2-}$ group with site symmetry 2 and metal–halide distances of 2.2280 (9) and 2.2833 (10) Å and Cl–Ni–Cl bond angles ranging from 98.06 (6) to 115.62 (4)°. The 4-chloropyridinium cation is located in general position and planar within error. A displacement ellipsoid plot of the ionic constituents is given in Fig. 1. Fig. 2 shows the classical hydrogen bonds and the short interhalogen contacts (dashed red lines, Cl \cdots Cl = 3.3762 (16) Å). Shortest interatomic distances between neighbouring cations amount to *ca* 3.5 Å and indicate π interactions. A projection of the unit cell is provided in Fig. 3. The above-mentioned contacts and the classical N–H \cdots Cl bonds result in a chain which extends in [101] direction. Adjacent strands are crosslinked by additional weak non-classical H bonds.

Experimental

2.0 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (476 mg) were dissolved in *ca* 10 ml conc hydrochloric acid. 4.0 mmol 4-chloropyridine (600 mg) in 2 ml H_2O were added. The mixture was stirred at room temp for 1 h. After several days of isothermal evaporation, 1.9 mmol, 816 mg of the product were obtained, corresp to yield of 95%.

The product does not melt but decomposes at temperatures above 443 K. At this temperature, pyridine may be sublimed off under vacuum.

Microanalytical data, found: C 27.14, H 2.71, N 6.37%. Calculated for $\text{C}_{10}\text{H}_{10}\text{Cl}_6\text{N}_2\text{Ni}$: C 27.96, H 2.35, N 6.52%.

Refinement

All H atoms were placed in idealized positions and treated as riding atoms with C–H distance of 0.93 Å and N–H distance of 0.86 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

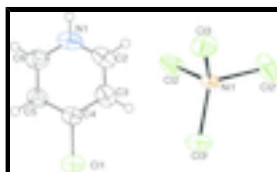


Fig. 1. Displacement ellipsoid plot (50% probability level) of the cation (left) and anion in the title compound; symmetry code: $i = 1 - x, y, 1.5 - z$.

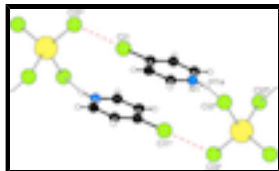


Fig. 2. Closest intermolecular interactions between cations and anions; hydrogen bonds and Cl...Cl contacts are drawn as dashed lines. Symmetry codes: ii = 1 - x, -y, 1 - z; iii = x, -y, z - 1/2; iv = x - 1/2, y + 1/2, z; v = 0.5 - x, 0.5 - y, 1 - z.

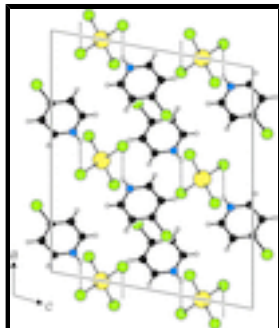


Fig. 3. Packing diagram of the title compound. Shortest interactions (shown in Fig. 2) extend along [101].

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β = 100.526 (3)°

V = 1650.0 (4) Å³

Z = 4

F(000) = 856

D_x = 1.729 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 5779 reflections

θ = 2.5–28.3°

μ = 2.13 mm⁻¹

T = 298 K

Block, light green

0.36 × 0.28 × 0.26 mm

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Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

graphite

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 1999)

T_{min} = 0.46, *T_{max}* = 0.57

5779 measured reflections

2049 independent reflections

1820 reflections with *I* > 2σ(*I*)

R_{int} = 0.026

θ_{max} = 28.3°, θ_{min} = 2.5°

h = -12→22

k = -9→9

l = -16→18

Refinement

Refinement on *F*²

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.045$$

$$wR(F^2) = 0.123$$

$$S = 1.07$$

2049 reflections

87 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 3.4552P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.98 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.04605 (7)	0.7500	0.03657 (17)
Cl1	0.23687 (6)	0.54295 (11)	0.57163 (7)	0.0551 (2)
N1	0.4043 (2)	0.3152 (4)	0.3908 (3)	0.0575 (8)
H1	0.4372	0.2717	0.3553	0.069*
C6	0.3310 (2)	0.3788 (5)	0.3468 (3)	0.0561 (8)
H6A	0.3162	0.3745	0.2792	0.067*
C5	0.2776 (2)	0.4503 (4)	0.4014 (3)	0.0488 (7)
H5A	0.2262	0.4942	0.3719	0.059*
C4	0.30238 (19)	0.4555 (4)	0.5012 (2)	0.0425 (6)
C3	0.3784 (2)	0.3868 (5)	0.5454 (3)	0.0557 (8)
H3A	0.3947	0.3887	0.6129	0.067*
C2	0.4285 (2)	0.3161 (5)	0.4867 (3)	0.0604 (9)
H2A	0.4798	0.2685	0.5141	0.072*
Cl2	0.42552 (5)	-0.15941 (15)	0.64578 (9)	0.0716 (3)
Cl3	0.59081 (7)	0.21312 (15)	0.68764 (8)	0.0692 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0316 (3)	0.0336 (3)	0.0470 (3)	0.000	0.0137 (2)	0.000
Cl1	0.0570 (5)	0.0507 (5)	0.0633 (5)	0.0008 (4)	0.0259 (4)	-0.0050 (3)
N1	0.0537 (17)	0.0489 (15)	0.077 (2)	0.0035 (13)	0.0319 (16)	-0.0008 (14)
C6	0.063 (2)	0.0528 (18)	0.0570 (18)	0.0012 (17)	0.0217 (16)	0.0033 (15)

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C5	0.0463 (17)	0.0456 (16)	0.0560 (18)	0.0044 (13)	0.0130 (14)	0.0072 (13)
C4	0.0402 (15)	0.0360 (14)	0.0538 (16)	-0.0028 (11)	0.0146 (13)	-0.0009 (12)
C3	0.0510 (19)	0.0515 (18)	0.062 (2)	0.0024 (15)	0.0026 (16)	0.0000 (16)
C2	0.0416 (17)	0.0540 (19)	0.085 (3)	0.0063 (15)	0.0112 (17)	-0.0002 (18)
Cl2	0.0384 (4)	0.0777 (6)	0.0951 (7)	0.0017 (4)	0.0026 (4)	-0.0373 (6)
Cl3	0.0636 (6)	0.0751 (6)	0.0769 (6)	-0.0151 (5)	0.0337 (5)	0.0112 (5)

Geometric parameters (\AA , $^\circ$)

Ni1—Cl3	2.2280 (9)	C6—C5	1.368 (5)
Ni1—Cl3 ⁱ	2.2280 (9)	C6—H6A	0.9300
Ni1—Cl2	2.2833 (10)	C5—C4	1.379 (5)
Ni1—Cl2 ⁱ	2.2833 (10)	C5—H5A	0.9300
Cl1—C4	1.712 (3)	C4—C3	1.387 (5)
N1—C2	1.324 (5)	C3—C2	1.368 (5)
N1—C6	1.336 (5)	C3—H3A	0.9300
N1—H1	0.8600	C2—H2A	0.9300
Cl3—Ni1—Cl3 ⁱ	113.76 (6)	C6—C5—C4	118.0 (3)
Cl3—Ni1—Cl2	115.62 (4)	C6—C5—H5A	121.0
Cl3 ⁱ —Ni1—Cl2	106.51 (4)	C4—C5—H5A	121.0
Cl3—Ni1—Cl2 ⁱ	106.51 (4)	C5—C4—C3	121.1 (3)
Cl3 ⁱ —Ni1—Cl2 ⁱ	115.62 (4)	C5—C4—Cl1	119.2 (3)
Cl2—Ni1—Cl2 ⁱ	98.06 (6)	C3—C4—Cl1	119.6 (3)
C2—N1—C6	122.9 (3)	C2—C3—C4	117.8 (3)
C2—N1—H1	118.5	C2—C3—H3A	121.1
C6—N1—H1	118.5	C4—C3—H3A	121.1
N1—C6—C5	119.9 (3)	N1—C2—C3	120.2 (3)
N1—C6—H6A	120.1	N1—C2—H2A	119.9
C5—C6—H6A	120.1	C3—C2—H2A	119.9

Symmetry codes: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2A \cdots Cl3	0.93	2.79	3.586 (4)	145.
N1—H1 \cdots Cl2 ⁱⁱ	0.86	2.41	3.158 (3)	145.
C5—H5A \cdots Cl2 ⁱⁱⁱ	0.93	2.75	3.633 (4)	159.

Symmetry codes: (ii) $-x+1, -y, -z+1$; (iii) $-x+1/2, -y+1/2, -z+1$.

Fig. 1

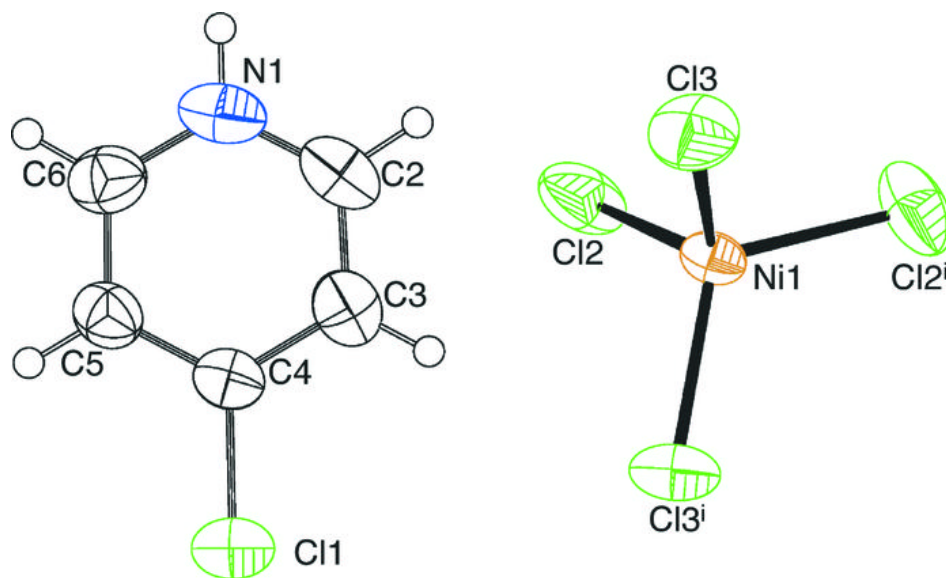


Fig. 2

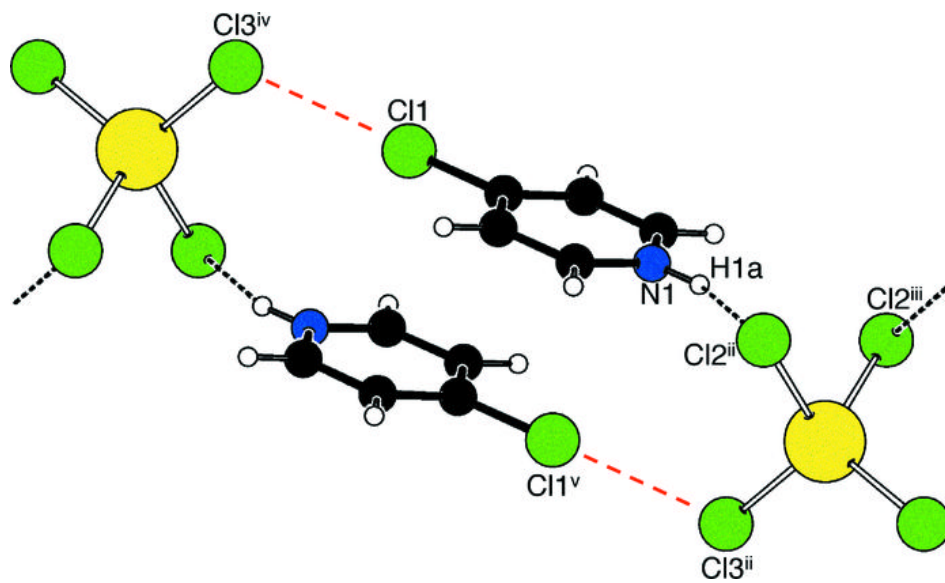


Fig. 3

