

Bis(4,4'-sulfanedioldipyridinium) tetra-chloridonickelate(II) dichloride

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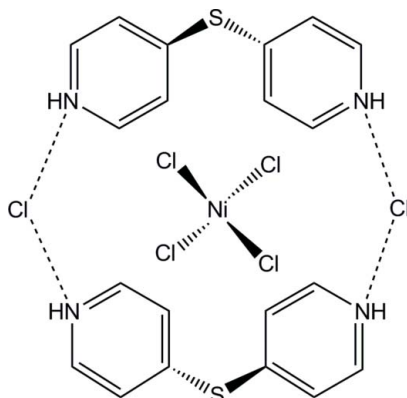
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 Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.037; wR factor = 0.084; data-to-parameter ratio = 20.9.

In the title compound, $(\text{C}_{10}\text{H}_{10}\text{N}_2\text{S})_2[\text{NiCl}_4]\text{Cl}_2$, the Ni^{2+} cation is tetrahedrally coordinated by four chloride anions. Two 4,4'-sulfanedioldipyridinium cations and two non-coordinating chloride anions are connected *via* $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen-bonding interactions into 20-membered rings, in the middle of which are situated the $[\text{NiCl}_4]^{2-}$ complex anions. These rings are stacked in the b -axis direction. The Ni^{2+} cation is located on a twofold rotation axis, whereas the chloride anions and the 4,4'-sulfanedioldipyridinium cations occupy general positions.

Related literature

For background information on this project, see: Boeckmann & Näther (2010, 2011); Wöhlert *et al.* (2011). For the crystal structure of 4,4'-thiodipyridine, see: Vaganova *et al.* (2004).



Experimental

Crystal data

 $(\text{C}_{10}\text{H}_{10}\text{N}_2\text{S})_2[\text{NiCl}_4]\text{Cl}_2$
 $M_r = 651.93$

 Monoclinic, $C2/c$
 $a = 19.0497$ (9) Å

 $b = 8.0534$ (5) Å
 $c = 17.7883$ (11) Å
 $\beta = 92.368$ (6)°
 $V = 2726.7$ (3) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 1.47$ mm⁻¹
 $T = 200$ K
 $0.32 \times 0.13 \times 0.07$ mm

Data collection

 Stoe IPDS-1 diffractometer
 Absorption correction: numerical
 (X -SHAPE and X -RED32; Stoe & Cie, 2008)
 $T_{\min} = 0.789$, $T_{\max} = 0.899$

 10707 measured reflections
 3162 independent reflections
 2308 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.084$
 $S = 0.99$
 3162 reflections

 151 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.43$ e Å⁻³
Table 1

Selected bond lengths (Å).

Ni1—Cl1	2.2569 (7)	Ni1—Cl2	2.2706 (6)
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Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N2—H1N2 \cdots Cl3 ⁱ	0.88	2.12	2.987 (3)	168
N1—H1N1 \cdots Cl3	0.88	2.32	3.078 (3)	144

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

Data collection: X -AREA (Stoe & Cie, 2008); cell refinement: X -AREA; data reduction: X -AREA; program(s) used to solve structure: $SHELXS97$ (Sheldrick, 2008); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 2008); molecular graphics: XP in $SHELXTL$ (Sheldrick, 2008) and $DIAMOND$ (Brandenburg, 2011); software used to prepare material for publication: $pubCIF$ (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2703).

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supporting information

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Bis(4,4'-sulfaneyldipyridinium) tetrachloridonickelate(II) dichloride

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S1. Comment

The title compound was prepared within a project on the synthesis and properties of transition metal thiocyanato coordination polymers (Boeckmann & Näther, 2010, 2011; Wöhlert *et al.*, 2011). During our attempts to prepare a one-dimensional coordination polymer based on 4-chloropyridine as a co-ligand, crystals of the title compound, $(C_{10}H_{10}N_2S^+)_2[NiCl_4]Cl_2$ (I), have been obtained accidentally and were characterized by single crystal X-ray diffraction.

In the crystal structure of (I) the Ni^{2+} cation is coordinated by four chloride anions within a slightly distorted tetrahedral coordination environment. The complex $[NiCl_4]^{2-}$ anions are surrounded by two 4,4'-sulfaneyldipyridinium cations and two chloride counter-anions (Fig. 1 and Table 1). Intermolecular N—H \cdots Cl hydrogen bonding is found between the 4,4'-sulfaneyldipyridinium cations and the non-coordinating chloride anions, which leads to the formation of 20-membered rings (Fig. 2 and Table 2). These rings are stacked in the direction of the *b* axis.

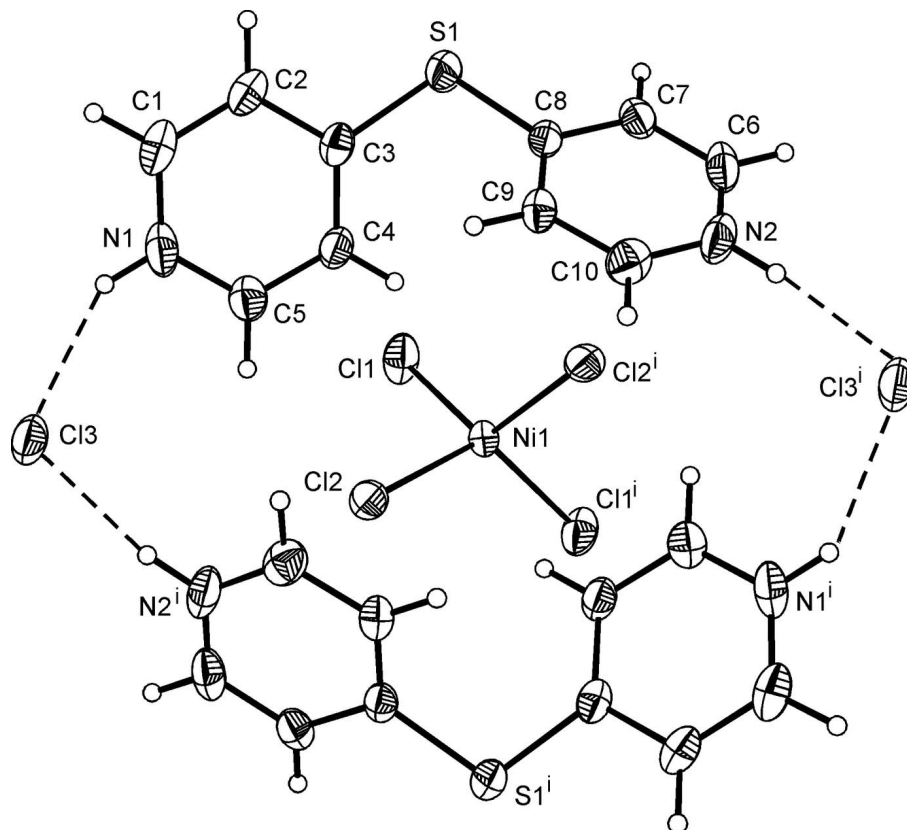
The dihedral angle between the pyridine rings in the cations amounts to $52.57(7)^\circ$. The corresponding bond lengths and angles are comparable to those in the neutral 4,4'-thiodipyridine molecule. Slight differences are found with respect to the dihedral angle between the pyridine rings which amounts to 65.4° in the neutral molecule (Vaganova *et al.*, 2004).

S2. Experimental

Barium thiocyanate trihydrate and 4-chloropyridine hydrochloride were purchased from Alfa Aesar, $Ni(SO_4)_2 \cdot 6H_2O$ was obtained from Merck. $Ni(NCS)_2$ was prepared by stirring $Ba(NCS)_2 \cdot 3H_2O$ (17.5 g, 56.9 mmol) and $NiSO_4 \cdot 6H_2O$ (15.0 g, 57 mmol) in water (500 mL). The white residue of $BaSO_4$ was filtered off and the solution evaporated using a rotary evaporator. The homogeneity of the product was investigated by X-ray powder diffraction. The title compound was prepared by the reaction of 26.2 mg $Ni(NCS)_2$ (0.15 mmol) and 97.5 mg 4-chloropyridine hydrochloride (0.60 mmol) in 1.5 mL ethanol at 354 K in a closed 10 mL glass culture tube. After one day blue needles of the title compound were obtained. The formation of 4,4'-thiodipyridine starting from 4-chloropyridine in an SCN $^-$ -containing environment and the presence of free Cl^- and complex $[NiCl_4]^{2-}$ anions seem to be a result of cleavage reactions of both the 4-chloropyridine and SCN $^-$ anions. However, the exact mechanism is unclear.

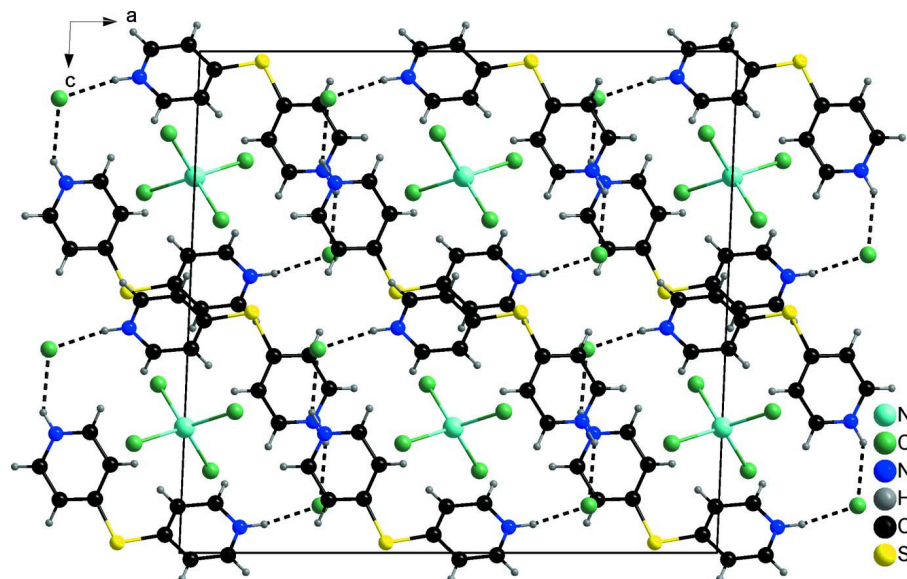
S3. Refinement

The aromatic H atoms (C- and N-bound) were located in a difference map but were positioned with idealized geometries and were refined isotropically with $U_{iso}(H) = 1.2 \cdot U_{eq}(C,N)$ using a riding model approximation with C—H = 0.95 Å and N—H = 0.88 Å.

**Figure 1**

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level.

[Symmetry code: $i = -x+1, y, -z+3/2.$]

**Figure 2**

Crystal structure of the title compound in a view along the b -axis. N—H \cdots Cl hydrogen bonding is shown as dashed lines.

Bis(4,4'-sulfanedioldipyridinium) tetrachloridonickelate(II) dichloride

Crystal data

 $(C_{10}H_{10}N_2S)_2[NiCl_4]Cl_2$ $M_r = 651.93$ Monoclinic, $C2/c$ Hall symbol: $-C\ 2yc$ $a = 19.0497\ (9)\ \text{\AA}$ $b = 8.0534\ (5)\ \text{\AA}$ $c = 17.7883\ (11)\ \text{\AA}$ $\beta = 92.368\ (6)^\circ$ $V = 2726.7\ (3)\ \text{\AA}^3$ $Z = 4$ $F(000) = 1320$ $D_x = 1.588\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 10707 reflections

 $\theta = 2.3\text{--}27.9^\circ$ $\mu = 1.47\ \text{mm}^{-1}$ $T = 200\ \text{K}$

Needle, blue

 $0.32 \times 0.13 \times 0.07\ \text{mm}$

Data collection

Stoe IPDS-1

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Phi scans

Absorption correction: numerical

 $(X\text{-SHAPE and X-RED32; Stoe \& Cie, 2008})$ $T_{\min} = 0.789, T_{\max} = 0.899$

10707 measured reflections

3162 independent reflections

2308 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.062$ $\theta_{\max} = 27.9^\circ, \theta_{\min} = 2.3^\circ$ $h = -23 \rightarrow 22$ $k = -10 \rightarrow 10$ $l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.084$ $S = 0.99$

3162 reflections

151 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-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.47\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.43\ \text{e \AA}^{-3}$ Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0013 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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	0.66427 (5)	0.7500	0.02527 (13)
Cl1	0.59273 (4)	0.81985 (9)	0.71816 (4)	0.0465 (2)
Cl2	0.55194 (4)	0.49082 (8)	0.83619 (3)	0.03563 (17)

Cl3	0.75812 (4)	0.08791 (10)	0.90585 (4)	0.04236 (19)
N1	0.73877 (13)	0.1738 (3)	0.73764 (14)	0.0425 (6)
H1N1	0.7637	0.1582	0.7798	0.051*
C1	0.76591 (16)	0.1281 (4)	0.67229 (18)	0.0424 (7)
H1	0.8121	0.0839	0.6718	0.051*
C2	0.72674 (14)	0.1451 (3)	0.60598 (16)	0.0366 (6)
H2	0.7444	0.1073	0.5598	0.044*
C3	0.66077 (14)	0.2189 (3)	0.60792 (14)	0.0305 (5)
C4	0.63496 (14)	0.2699 (3)	0.67604 (14)	0.0319 (5)
H4	0.5905	0.3227	0.6779	0.038*
C5	0.67510 (14)	0.2424 (3)	0.74071 (15)	0.0351 (6)
H5	0.6575	0.2724	0.7880	0.042*
S1	0.61640 (4)	0.26112 (10)	0.52047 (4)	0.03808 (18)
N2	0.38935 (13)	0.1530 (3)	0.55137 (14)	0.0394 (5)
H1N2	0.3443	0.1351	0.5570	0.047*
C6	0.40903 (15)	0.2520 (4)	0.49540 (15)	0.0383 (6)
H6	0.3746	0.2986	0.4615	0.046*
C7	0.47845 (14)	0.2859 (3)	0.48701 (14)	0.0313 (5)
H7	0.4926	0.3573	0.4479	0.038*
C8	0.52829 (13)	0.2148 (3)	0.53643 (13)	0.0262 (5)
C9	0.50641 (14)	0.1074 (3)	0.59261 (14)	0.0284 (5)
H9	0.5398	0.0541	0.6257	0.034*
C10	0.43635 (15)	0.0807 (3)	0.59898 (15)	0.0357 (6)
H10	0.4206	0.0100	0.6376	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0281 (3)	0.0202 (2)	0.0271 (2)	0.000	-0.00296 (16)	0.000
Cl1	0.0355 (4)	0.0461 (4)	0.0574 (4)	-0.0070 (3)	-0.0039 (3)	0.0256 (3)
Cl2	0.0370 (4)	0.0359 (3)	0.0341 (3)	0.0052 (3)	0.0038 (2)	0.0137 (3)
Cl3	0.0275 (4)	0.0549 (4)	0.0440 (4)	0.0065 (3)	-0.0057 (3)	-0.0111 (3)
N1	0.0347 (15)	0.0451 (13)	0.0462 (14)	0.0034 (11)	-0.0153 (10)	-0.0021 (11)
C1	0.0290 (17)	0.0392 (16)	0.0586 (19)	0.0058 (11)	-0.0034 (12)	0.0004 (13)
C2	0.0266 (15)	0.0371 (15)	0.0462 (15)	0.0021 (11)	0.0050 (10)	-0.0019 (12)
C3	0.0248 (14)	0.0302 (12)	0.0365 (13)	-0.0030 (9)	-0.0002 (9)	0.0021 (10)
C4	0.0256 (14)	0.0339 (13)	0.0359 (13)	0.0016 (10)	-0.0006 (9)	-0.0040 (10)
C5	0.0351 (16)	0.0326 (13)	0.0372 (14)	0.0001 (11)	-0.0035 (10)	-0.0023 (11)
S1	0.0278 (4)	0.0548 (4)	0.0316 (3)	-0.0045 (3)	0.0014 (2)	0.0041 (3)
N2	0.0240 (13)	0.0422 (13)	0.0520 (14)	-0.0035 (10)	-0.0005 (9)	-0.0154 (11)
C6	0.0339 (16)	0.0375 (14)	0.0421 (15)	0.0076 (12)	-0.0139 (11)	-0.0110 (12)
C7	0.0360 (16)	0.0305 (13)	0.0269 (12)	0.0033 (10)	-0.0051 (9)	-0.0018 (9)
C8	0.0265 (13)	0.0239 (11)	0.0280 (11)	0.0017 (9)	-0.0005 (9)	-0.0082 (9)
C9	0.0282 (14)	0.0236 (11)	0.0330 (12)	0.0000 (9)	-0.0039 (9)	-0.0021 (9)
C10	0.0384 (17)	0.0292 (13)	0.0397 (14)	-0.0060 (11)	0.0038 (11)	-0.0047 (11)

Geometric parameters (Å, °)

Ni1—C11	2.2569 (7)	C4—H4	0.9500
Ni1—C11 ⁱ	2.2569 (7)	C5—H5	0.9500
Ni1—C12 ⁱ	2.2706 (7)	S1—C8	1.754 (3)
Ni1—C12	2.2706 (6)	N2—C10	1.340 (4)
N1—C5	1.336 (4)	N2—C6	1.341 (4)
N1—C1	1.343 (4)	N2—H1N2	0.8800
N1—H1N1	0.8800	C6—C7	1.365 (4)
C1—C2	1.376 (4)	C6—H6	0.9500
C1—H1	0.9500	C7—C8	1.391 (3)
C2—C3	1.392 (4)	C7—H7	0.9500
C2—H2	0.9500	C8—C9	1.398 (3)
C3—C4	1.389 (4)	C9—C10	1.361 (4)
C3—S1	1.772 (3)	C9—H9	0.9500
C4—C5	1.373 (4)	C10—H10	0.9500
C11—Ni1—C11 ⁱ	112.56 (5)	N1—C5—H5	119.7
C11—Ni1—C12 ⁱ	119.73 (3)	C4—C5—H5	119.7
C11 ⁱ —Ni1—C12 ⁱ	100.79 (2)	C8—S1—C3	104.00 (12)
C11—Ni1—C12	100.79 (2)	C10—N2—C6	121.9 (3)
C11 ⁱ —Ni1—C12	119.73 (3)	C10—N2—H1N2	119.1
C12 ⁱ —Ni1—C12	104.07 (4)	C6—N2—H1N2	119.1
C5—N1—C1	122.1 (2)	N2—C6—C7	120.1 (2)
C5—N1—H1N1	119.0	N2—C6—H6	119.9
C1—N1—H1N1	119.0	C7—C6—H6	119.9
N1—C1—C2	120.0 (3)	C6—C7—C8	119.2 (3)
N1—C1—H1	120.0	C6—C7—H7	120.4
C2—C1—H1	120.0	C8—C7—H7	120.4
C1—C2—C3	118.7 (3)	C7—C8—C9	119.4 (2)
C1—C2—H2	120.7	C7—C8—S1	116.3 (2)
C3—C2—H2	120.7	C9—C8—S1	124.26 (19)
C4—C3—C2	120.0 (2)	C10—C9—C8	118.6 (2)
C4—C3—S1	122.4 (2)	C10—C9—H9	120.7
C2—C3—S1	117.3 (2)	C8—C9—H9	120.7
C5—C4—C3	118.6 (3)	N2—C10—C9	120.7 (3)
C5—C4—H4	120.7	N2—C10—H10	119.7
C3—C4—H4	120.7	C9—C10—H10	119.7
N1—C5—C4	120.5 (3)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H1N2 \cdots C13 ⁱ	0.88	2.12	2.987 (3)	168
N1—H1N1 \cdots C13	0.88	2.32	3.078 (3)	144

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