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Chlorido[1-(4,5-dihydro-1,3-thiazol-2-yl-κN)ethanone thiosemicarbazonato-κ^2N^1,S]nickel(II)

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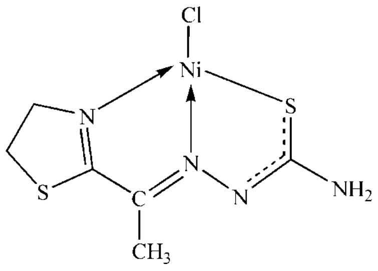
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.034; wR factor = 0.076; data-to-parameter ratio = 20.0.

In the title compound, $[Ni(C_6H_9N_4S_2)Cl]$, the Ni atom is in a slightly distorted square-planar environment coordinated by a Cl atom and a deprotonated thiosemicarbazone ligand *via* its thiazoline N, azomethine N and thiolate S atoms. Short intermolecular N—H⋯Cl and C—H⋯S contacts are present in the crystal structure.

Related literature

For the structure of the organic ligand and several metal complexes, see: Viñuelas-Zahínos *et al.* (2011). For the structures of closely related nickel complexes, see: Liu *et al.* (1999); Philip *et al.* (2004); Swearingen *et al.* (2002).



Experimental

Crystal data

$[Ni(C_6H_9N_4S_2)Cl]$
M_r = 295.45
Monoclinic, $P2_1/c$
a = 9.656 (2) Å
b = 10.617 (2) Å
c = 11.187 (3) Å
β = 112.874 (4)°
V = 1056.7 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.45 mm^{-1}
T = 298 K
0.22 × 0.15 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.615, T_{max} = 0.828
2554 measured reflections
2554 independent reflections
1758 reflections with $2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.076
S = 1.05
2554 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H4B⋯Cl^{i}	0.86	2.51	3.310 (3)	155
N4—H4A⋯Cl^{ii}	0.86	2.53	3.373 (3)	166
C3—H3B⋯S1^{iii}	0.97	2.98	3.537 (3)	118

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2251).

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supplementary materials

Acta Cryst. (2011). E**67**, m79 [**doi:10.1107/S1600536810051500**]

Chlorido[1-(4,5-dihydro-1,3-thiazol-2-yl-*κN*)ethanone thiosemicarbazonato-κ^2N^1,*S*]nickel(II)

E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García and Á. Bernalte-García

Comment

The preceding study reports the metal complexes of 1–(4,5–dihydro–1,3–thiazol–2–yl)ethanone thiosemicarbazone (HATtsc) (Viñuelas–Zahínos *et al.*, 2011). It should be pointed out that in nickel complex the organic ligand is deprotonated and shifts from the thione to the thiolate form, in such a way that the negative charge is delocalized between the two bonds S2—C6 and N3—C6, as it is observed in other nickel complexes with thiosemicarbazone ligands (Liu *et al.*, 1999; Philip *et al.*, 2004; Swearingen *et al.*, 2002). Another difference in complex with respect to the structure of the free ligand HATtsc is the degree of rotation around the C1—C4 and C6—N3 bonds, which permits coordination through N1 and S2. In crystal structure there are the following short intermolecular contacts: N4—H4A···Cl, N4—H4B···Cl and C3—H3B···S1.

Experimental

1-(4,5-dihydro-1,3-thiazol-2-yl)ethanone thiosemicarbazone (HATtsc) was synthesized as according to a literature procedure (Viñuelas-Zahínos *et al.*, 2010). A solution containing $NiCl_2{\cdot}6H_2O$ (58.5 mg, 0.25 mmol) in 1 ml ethanol:acetonitrile (2:1) was added to a solution (40 ml) of HATtsc (50.0 mg, 0.25 mmol) in ethanol:acetonitrile (2:1). The brown product was recrystallized from ethanol:methanol (1:1) to give brown crystals.

Refinement

All hydrogen atoms attached to carbon and nitrogen atoms were positioned geometrically and refined as riding, with C—H = 0.96–0.97Å, N—H = 0.86Å and U_{iso}(H) = 1.2(1.5 for methyl group) U_{eq}(C,N).

Figures

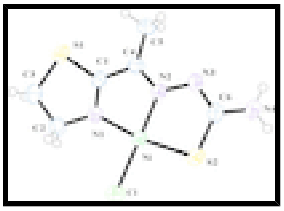

Fig. 1. A view of molecular structure of title compound, showing the atom–numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

Chlorido[1-(4,5-dihydro-1,3-thiazol-2-yl-κ*N*)ethanone thiosemicarbazonato-κ^2N^1,*S*]nickel(II)

Crystal data

$[Ni(C_6H_9N_4S_2)Cl]$

M_r = 295.45

Monoclinic, $P2_1/c$

$F(000)$ = 600

D_x = 1.857 Mg m^{-3}

Mo *K*α radiation, λ = 0.71073 Å

Hall symbol: -P 2ybc

$a = 9.656$ (2) Å

$b = 10.617$ (2) Å

$c = 11.187$ (3) Å

$\beta = 112.874$ (4)°

$V = 1056.7$ (4) Å^3

$Z = 4$

Cell parameters from 912 reflections

$\theta = 2.3$–26.3°

$\mu = 2.45$ mm^{-1}

$T = 298$ K

Prism, brown

0.22 × 0.15 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer

Radiation source: fine–focus sealed tube

graphite

ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)

$T_{\text{min}} = 0.615$, $T_{\text{max}} = 0.828$

2554 measured reflections

2554 independent reflections

1758 reflections with 2σ(I)

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 28.3$°, $\theta_{\text{min}} = 2.3$°

$h = -12 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.076$

$S = 1.05$

2554 reflections

128 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

$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.33$ e Å^{-3}

$\Delta\rho_{\text{min}} = -0.34$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3581 (3)	0.6235 (2)	0.0701 (2)	0.0334 (6)
C2	0.3833 (3)	0.4480 (2)	0.1999 (3)	0.0426 (7)
H2A	0.4210	0.4551	0.2936	0.051*
H2B	0.4086	0.3650	0.1783	0.051*
C3	0.2123 (3)	0.4657 (3)	0.1417 (3)	0.0504 (8)
H3A	0.1753	0.4759	0.2103	0.06*
H3B	0.1639	0.3926	0.0905	0.06*
C4	0.4210 (3)	0.7245 (2)	0.0176 (2)	0.0340 (6)
C5	0.3317 (3)	0.8206 (3)	−0.0777 (3)	0.0460 (7)
H5A	0.3662	0.9032	−0.0445	0.069*
H5B	0.2275	0.8121	−0.0919	0.069*
H5C	0.3438	0.8085	−0.1581	0.069*
C6	0.7922 (3)	0.7897 (2)	0.0918 (3)	0.0385 (6)
Cl	0.75176 (8)	0.43164 (6)	0.31254 (7)	0.0474 (2)
N1	0.4522 (2)	0.5445 (2)	0.1476 (2)	0.0361 (5)
N2	0.5671 (2)	0.71858 (19)	0.0663 (2)	0.0333 (5)
N3	0.6450 (2)	0.8074 (2)	0.0291 (2)	0.0399 (6)
N4	0.8837 (3)	0.8692 (2)	0.0669 (2)	0.0552 (7)
H4A	0.8472	0.9292	0.0121	0.066*
H4B	0.9795	0.8606	0.1057	0.066*
Ni	0.65556 (4)	0.58829 (3)	0.18229 (3)	0.03380 (12)
S1	0.17043 (8)	0.60537 (7)	0.03983 (8)	0.0493 (2)
S2	0.86881 (8)	0.66908 (7)	0.20402 (7)	0.0465 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0295 (14)	0.0359 (14)	0.0342 (15)	−0.0026 (11)	0.0119 (12)	−0.0042 (12)
C2	0.0445 (17)	0.0365 (15)	0.0506 (19)	−0.0033 (13)	0.0225 (15)	0.0017 (13)
C3	0.0422 (17)	0.0473 (17)	0.061 (2)	−0.0105 (14)	0.0187 (16)	0.0021 (15)
C4	0.0331 (15)	0.0317 (14)	0.0340 (15)	0.0010 (11)	0.0094 (12)	−0.0004 (11)
C5	0.0394 (16)	0.0458 (17)	0.0475 (18)	0.0044 (13)	0.0112 (14)	0.0105 (14)
C6	0.0358 (15)	0.0396 (15)	0.0441 (17)	−0.0061 (12)	0.0199 (13)	−0.0028 (13)
Cl	0.0398 (4)	0.0440 (4)	0.0541 (5)	0.0087 (3)	0.0137 (3)	0.0101 (3)
N1	0.0314 (12)	0.0359 (12)	0.0403 (13)	−0.0027 (10)	0.0131 (10)	0.0025 (10)
N2	0.0303 (12)	0.0333 (12)	0.0369 (13)	−0.0006 (9)	0.0137 (10)	0.0004 (10)
N3	0.0393 (13)	0.0383 (13)	0.0458 (14)	−0.0047 (10)	0.0206 (12)	0.0030 (11)
N4	0.0351 (14)	0.0576 (16)	0.0727 (19)	−0.0084 (12)	0.0207 (13)	0.0112 (14)
Ni	0.02818 (19)	0.03349 (19)	0.0382 (2)	0.00139 (15)	0.01121 (15)	0.00176 (15)
S1	0.0281 (4)	0.0485 (5)	0.0661 (5)	−0.0031 (3)	0.0126 (4)	0.0033 (4)
S2	0.0293 (4)	0.0486 (4)	0.0578 (5)	−0.0008 (3)	0.0128 (3)	0.0060 (4)

Geometric parameters (Å, °)

C1—N1	1.292 (3)	C5—H5B	0.96

C1—C4	1.463 (3)	C5—H5C	0.96
C1—S1	1.720 (3)	C6—N4	1.327 (3)
C2—N1	1.462 (3)	C6—N3	1.332 (3)
C2—C3	1.533 (4)	C6—S2	1.743 (3)
C2—H2A	0.97	Cl—Ni	2.1679 (8)
C2—H2B	0.97	N1—Ni	1.905 (2)
C3—S1	1.817 (3)	N2—N3	1.367 (3)
C3—H3A	0.97	N2—Ni	1.861 (2)
C3—H3B	0.97	N4—H4A	0.86
C4—N2	1.302 (3)	N4—H4B	0.86
C4—C5	1.485 (3)	Ni—S2	2.1554 (9)
C5—H5A	0.96		

N1—C1—C4	116.9 (2)	H5B—C5—H5C	109.5
N1—C1—S1	118.2 (2)	N4—C6—N3	117.4 (3)
C4—C1—S1	124.9 (2)	N4—C6—S2	119.2 (2)
N1—C2—C3	109.1 (2)	N3—C6—S2	123.4 (2)
N1—C2—H2A	109.9	C1—N1—C2	114.4 (2)
C3—C2—H2A	109.9	C1—N1—Ni	112.27 (18)
N1—C2—H2B	109.9	C2—N1—Ni	133.07 (18)
C3—C2—H2B	109.9	C4—N2—N3	118.3 (2)
H2A—C2—H2B	108.3	C4—N2—Ni	117.17 (18)
C2—C3—S1	107.85 (19)	N3—N2—Ni	124.56 (16)
C2—C3—H3A	110.1	C6—N3—N2	110.0 (2)
S1—C3—H3A	110.1	C6—N4—H4A	120
C2—C3—H3B	110.1	C6—N4—H4B	120
S1—C3—H3B	110.1	H4A—N4—H4B	120
H3A—C3—H3B	108.4	N2—Ni—N1	83.24 (9)
N2—C4—C1	110.4 (2)	N2—Ni—S2	86.68 (7)
N2—C4—C5	124.5 (2)	N1—Ni—S2	169.68 (7)
C1—C4—C5	125.2 (2)	N2—Ni—Cl	177.76 (7)
C4—C5—H5A	109.5	N1—Ni—Cl	95.06 (7)
C4—C5—H5B	109.5	S2—Ni—Cl	95.08 (3)
H5A—C5—H5B	109.5	C1—S1—C3	90.43 (13)
C4—C5—H5C	109.5	C6—S2—Ni	95.27 (9)
H5A—C5—H5C	109.5		

N1—C2—C3—S1	−3.3 (3)	C4—N2—Ni—N1	0.65 (19)
N1—C1—C4—N2	−3.2 (3)	N3—N2—Ni—N1	−179.2 (2)
S1—C1—C4—N2	174.88 (19)	C4—N2—Ni—S2	−177.17 (19)
N1—C1—C4—C5	176.9 (2)	N3—N2—Ni—S2	3.02 (19)
S1—C1—C4—C5	−5.1 (4)	C1—N1—Ni—N2	−2.43 (19)
C4—C1—N1—C2	178.3 (2)	C2—N1—Ni—N2	−175.7 (3)
S1—C1—N1—C2	0.1 (3)	C1—N1—Ni—S2	9.8 (5)
C4—C1—N1—Ni	3.7 (3)	C2—N1—Ni—S2	−163.5 (3)
S1—C1—N1—Ni	−174.50 (12)	C1—N1—Ni—Cl	179.02 (18)
C3—C2—N1—C1	2.2 (3)	C2—N1—Ni—Cl	5.7 (2)
C3—C2—N1—Ni	175.34 (19)	N1—C1—S1—C3	−1.9 (2)
C1—C4—N2—N3	−179.1 (2)	C4—C1—S1—C3	−179.9 (2)
C5—C4—N2—N3	0.8 (4)	C2—C3—S1—C1	2.9 (2)

C1—C4—N2—Ni	−1.1 (3)	N4—C6—S2—Ni	−178.7 (2)
C5—C4—N2—Ni	−179.0 (2)	N3—C6—S2—Ni	1.6 (2)
N4—C6—N3—N2	−179.5 (2)	N2—Ni—S2—C6	−2.03 (11)
S2—C6—N3—N2	0.1 (3)	N1—Ni—S2—C6	−14.2 (4)
C4—N2—N3—C6	177.7 (2)	Cl—Ni—S2—C6	176.58 (9)
Ni—N2—N3—C6	−2.5 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4B···Cl^{i}	0.86	2.51	3.310 (3)	155.
N4—H4A···Cl^{ii}	0.86	2.53	3.373 (3)	166.
C3—H3B···S1^{iii}	0.97	2.98	3.537 (3)	118.

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

Fig. 1