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## Structure Reports

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# Chlorido[1-(4,5-dihydro-1,3-thiazol-2-yl- $\kappa$ N)ethanone thiosemicarbazonato- $\kappa^2$ N<sup>1</sup>,S]nickel(II)

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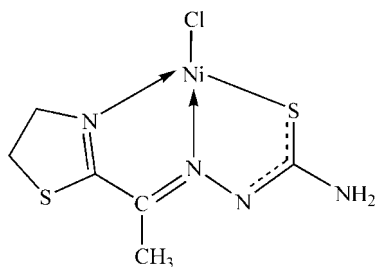
Received 22 November 2010; accepted 8 December 2010

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.076; data-to-parameter ratio = 20.0.

In the title compound,  $[\text{Ni}(\text{C}_6\text{H}_9\text{N}_4\text{S}_2)\text{Cl}]$ , 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  $\text{N}-\text{H}\cdots\text{Cl}$  and  $\text{C}-\text{H}\cdots\text{S}$  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

 $[\text{Ni}(\text{C}_6\text{H}_9\text{N}_4\text{S}_2)\text{Cl}]$   
 $M_r = 295.45$   
 Monoclinic,  $P2_1/c$ 
 $a = 9.656$  (2) Å  
 $b = 10.617$  (2) Å  
 $c = 11.187$  (3) Å

 $\beta = 112.874$  (4)°  
 $V = 1056.7$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

 $\mu = 2.45$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.22 \times 0.15 \times 0.08$  mm

### Data collection

 Bruker SMART 1000 CCD diffractometer  
 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  $2\sigma(I)$   
 $R_{\text{int}} = 0.030$ 

### 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  
 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

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

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

The authors would like to thank the Junta de Extremadura (III PRI+D+I) and the FEDER (project PRI08A022) for support.

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

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## supporting information

*Acta Cryst.* (2011). E67, m79 [https://doi.org/10.1107/S1600536810051500]

## Chlorido[1-(4,5-dihydro-1,3-thiazol-2-yl- $\kappa$ N)ethanone thiosemicarbazonato- $\kappa^2$ N<sup>1</sup>,S]nickel(II)

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### S1. Comment

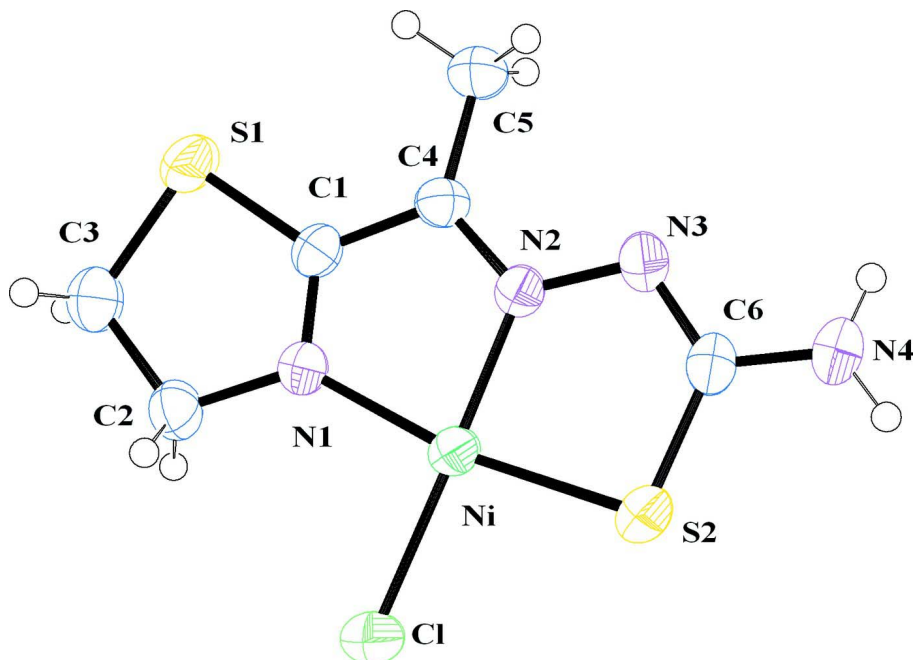
The preceding study reports the metal complexes of 1-(4,5-dihydro-1,3-thiazol-2-yl)ethanone thiosemicarbazone (HATtsc) (Viñuelas-Zahinos *et al.*, 2011). It should be pointed out that in nickel complex the organic ligand is deprotonated and shifts from the thione to the thiolate form, in such a way that 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 $\cdots$ Cl, N4—H4B $\cdots$ Cl and C3—H3B $\cdots$ S1.

### S2. Experimental

1-(4,5-dihydro-1,3-thiazol-2-yl)ethanone thiosemicarbazone (HATtsc) was synthesized as according to a literature procedure (Viñuelas-Zahinos *et al.*, 2010). A solution containing NiCl<sub>2</sub>·6H<sub>2</sub>O (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.

### S3. Refinement

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



**Figure 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- $\kappa$ N)ethanone thiosemicarbazonato- $\kappa^2$ N<sup>1</sup>,S]nickel(II)**

*Crystal data*

[Ni(C<sub>6</sub>H<sub>9</sub>N<sub>4</sub>S<sub>2</sub>)Cl]

$M_r = 295.45$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.656(2) \text{ \AA}$

$b = 10.617(2) \text{ \AA}$

$c = 11.187(3) \text{ \AA}$

$\beta = 112.874(4)^\circ$

$V = 1056.7(4) \text{ \AA}^3$

$Z = 4$

$F(000) = 600$

$D_x = 1.857 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 912 reflections

$\theta = 2.3\text{--}26.3^\circ$

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

$T = 298 \text{ K}$

Prism, brown

$0.22 \times 0.15 \times 0.08 \text{ mm}$

*Data collection*

Bruker SMART 1000 CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2004)

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

2554 measured reflections

2554 independent reflections

1758 reflections with  $2\sigma(I)$

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

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -12 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 14$

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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

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 ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ ,  $^\circ$ )

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 ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4B $\cdots$ Cl <sup>i</sup>	0.86	2.51	3.310 (3)	155
N4—H4A $\cdots$ Cl <sup>ii</sup>	0.86	2.53	3.373 (3)	166
C3—H3B $\cdots$ S1 <sup>iii</sup>	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)  $-x, -y+1, -z$ .