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## Key indicators

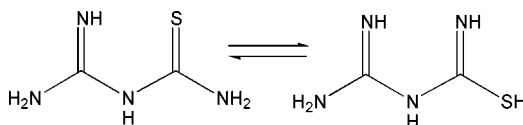
Single-crystal X-ray study  
T = 295 K  
Mean  $\sigma(\text{N}-\text{C}) = 0.006 \text{ \AA}$   
R factor = 0.053  
wR factor = 0.134  
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*cis*-Bis(amidinothioureato- $\kappa^2N,N'$ )nickel(II)

The title compound,  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{S})_2]$ , has a twofold axis. The  $\text{Ni}^{\text{II}}$  atom is coordinated in a deformed square-planar geometry by four imino N atoms of two atu ligands (Hatu = amidinothiourea). Two six-membered chelate rings including the Ni atom are twisted with a dihedral angle of  $17.24 (16)^\circ$ . The  $[\text{Ni}(\text{atu})_2]$  units make a two-dimensional layer *via*  $\text{N}-\text{H} \cdots \text{S}$  hydrogen bonds.

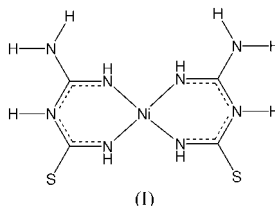
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## Comment

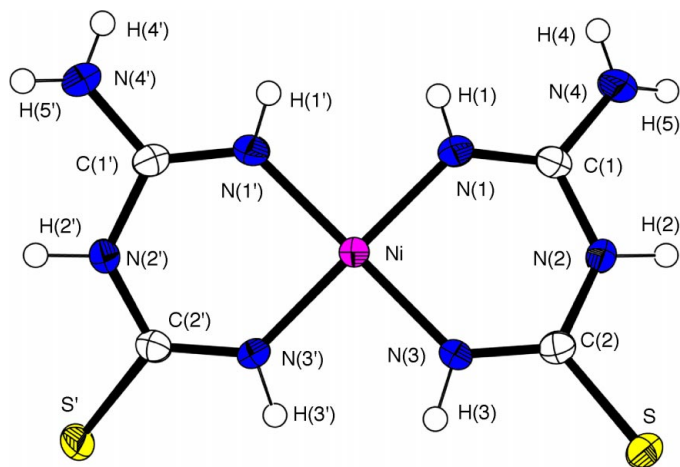
Amidinothiourea (Hatu) can be used to construct a metal-complex-based module for superstructures as it has available coordination sites (Vilar *et al.*, 1998). Moreover, SN donors stabilize the lower oxidation states of metal atoms and lower the electron density at NO in metal nitrosyls (Chakrabarty *et al.*, 1990).



Hatu has two tautomeric forms (see Scheme). It can coordinate to metal ions using either two N atoms (*N,N'*-chelating) or one N and one S atom (*N,S*-chelating). However, very few reports have been appeared on the Hatu ligand (Vilar *et al.*, 1998, 1999; Cheng *et al.*, 2001). Among them one report shows that Hatu is coordinated to  $\text{Ni}^{\text{II}}$  ion in an *N,N'*-chelating mode, to form a *trans* complex (Vilar *et al.*, 1999). During our studies on coordination compounds with Hatu, orange single crystals of the title compound, (I), were obtained. The crystal structure of (I) is presented here.



The crystal structure of (I) consists of a mononuclear complex  $\text{Ni}(\text{atu})_2$ . An *ORTEP*-3 (Farrugia, 1997) drawing with the atom-numbering scheme is shown in Fig. 1. The  $\text{Ni}^{\text{II}}$  atom is coordinated in a deformed square-planar geometry by four imino N atoms of two atu ligands. The two six-membered rings incorporating the Ni atom are twisted with a dihedral angle of  $17.24 (16)^\circ$ . The Ni—N distances are 1.860 (4) and 1.855 (4) Å



**Figure 1**  
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

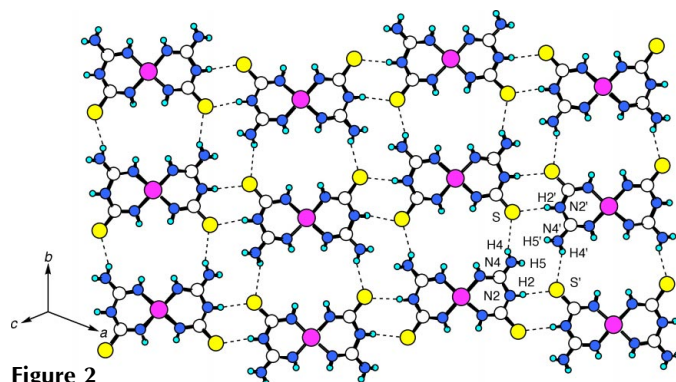
(Table 1). The shortness of the C–N bonds (1.29–1.37 Å) indicates the presence of multiple bonding with delocalization of  $\pi$  electrons. The coordination geometry of (I) is similar to that of  $[\text{Pd}(\text{atu})_2]\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$  (Chakrabarty *et al.*, 1990), but the coordinating atoms (*N,S*-chelating) are different in that case. On the other hand, *trans*-Ni(atu)<sub>2</sub> has the same coordinating atoms (*N,N'*-chelating) with similar Ni–N distances (Vilar *et al.*, 1999), but the crystal packing modes of the two compounds are different. The *cis* coordination mode in (I) has multi-site hydrogen-bonding ability that allows the mononuclear building module to form a hydrogen-bond-supported two-dimensional layer structure. Ni(atu)<sub>2</sub> molecules are connected to each other *via* hydrogen-bonding interactions, which are formed between terminal amino groups and S atoms, generating a straight tape along the *b* axis. The tapes are hydrogen bonded to form a two-dimensional layer perpendicular to the [101] direction (Fig. 2 and Table 2). The layers make a three-dimensional packing structure through stacking interactions (Fig. 3). The minimum distance between the layers (C...N) is 3.319 (6) Å.

## Experimental

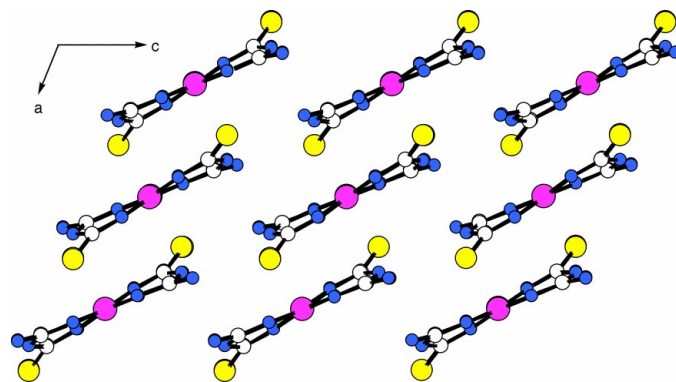
To a solution of nickel acetate monohydrate (0.019 g, 0.1 mmol) in H<sub>2</sub>O (5 ml), amidinothiurea (0.0236 g, 0.2 mmol) in methanol (5 ml) was added without mixing the two solutions. Orange crystals of (I) began to form at ambient temperature in two weeks. One of these crystals was used for X-ray crystallography. Calculated for C<sub>4</sub>H<sub>10</sub>N<sub>8</sub>NiS<sub>2</sub>: C 16.39, H 3.44, N 38.24%; found: C 16.35, H 3.36, N 37.93%.

### Crystal data

$[\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{S})_2]$	$D_x = 1.964 \text{ Mg m}^{-3}$
$M_r = 293.03$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 20 reflections
$a = 14.804 (2) \text{ \AA}$	$\theta = 2.5\text{--}10^\circ$
$b = 7.8988 (14) \text{ \AA}$	$\mu = 2.36 \text{ mm}^{-1}$
$c = 9.1216 (13) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 111.732 (12)^\circ$	Block, orange
$V = 990.8 (3) \text{ \AA}^3$	$0.2 \times 0.1 \times 0.1 \text{ mm}$
$Z = 4$	



**Figure 2**  
The layer structure of (I). H atoms have been omitted for clarity. The dashed lines represent hydrogen bonds.



**Figure 3**  
Projection of the crystal structure of (I) along the *b* axis.

### Data collection

MacScience MXC3 diffractometer	$R_{\text{int}} = 0.013$
$\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -19 \rightarrow 17$
$T_{\text{min}} = 0.753, T_{\text{max}} = 0.790$	$k = 0 \rightarrow 10$
1257 measured reflections	$l = 0 \rightarrow 11$
1141 independent reflections	3 standard reflections every 100 reflections
906 reflections with $I > 2\sigma(I)$	intensity decay: none

### Refinement

Refinement on $F^2$	Only coordinates of H atoms refined
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1140 reflections	$\Delta\rho_{\text{max}} = 0.80 \text{ e \AA}^{-3}$
84 parameters	$\Delta\rho_{\text{min}} = -0.66 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1–N3	1.855 (4)	N2–C2	1.360 (6)
Ni1–N1	1.860 (4)	N2–C1	1.368 (5)
S1–C2	1.726 (4)	N3–C2	1.302 (6)
N1–C1	1.288 (6)	N4–C1	1.350 (6)
N3–Ni1–N1	90.52 (17)	N1–C1–N4	124.6 (4)
N1–Ni1–N1 <sup>i</sup>	90.6 (2)	N1–C1–N2	121.7 (4)
N3–Ni1–N3 <sup>i</sup>	89.9 (2)	N4–C1–N2	113.7 (4)
C1–N1–Ni1	129.2 (3)	N3–C2–N2	119.6 (4)
C2–N2–C1	126.5 (4)	N3–C2–S1	124.0 (4)
C2–N3–Ni1	130.6 (3)	N2–C2–S1	116.4 (3)

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N4-H4 \cdots S1^i$	0.77 (6)	2.77 (6)	3.434 (5)	145 (5)
$N2-H2 \cdots S1^{ii}$	0.87 (6)	2.51 (6)	3.362 (4)	167 (5)

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

The H-atom coordinates were refined with a fixed  $U_{iso}$  value of  $0.031 \text{ \AA}^2$ .

Data collection: *CRYSTAN G* (MacScience, 1992); cell refinement: *CRYSTAN G*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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