

THE CRYSTAL CHEMISTRY OF NICKEL(II) COMPLEXES  
WITH THIOSEMICARBAZIDE  
THE CRYSTAL STRUCTURE  
OF DITHIOCYANATO-BIS(THIOSEMICARBAZIDE)NICKEL(II)

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The crystal structure of dithiocyanato-bis(thiosemicarbazide)-nickel (II),  $\text{Ni}(\text{NCS})_2(\text{CH}_5\text{N}_3\text{S})_2$ , was determined by means of the X-ray structure analysis. The space group is  $P2_1/c$ ; there are two molecules in the unit cell. Lattice constants:  $a$  5.300(4) Å,  $b$  7.761(5) Å,  $c$  16.12(2) Å,  $\beta$  92.01(6)°; density  $\rho_0$  1.77 g/cm<sup>3</sup>,  $\rho_c$  1.769 g/cm<sup>3</sup>. The crystal structure was solved by heavy-atom method using 590 independent reflexions measured photometrically from Weissenberg photographs. Both atomic coordinates and isotropic temperature factor coefficients were refined by the least-squares method the final  $R$ -factor value being 13.8% for observed reflections only. The nickel atom is coordinated octahedrally by four nitrogen and two sulphur atoms. The thiosemicarbazide molecule is bonded to the nickel atom as a chelate through the nitrogen atom of the hydrazine group (2.13(2) Å) and the sulphur atom (2.45(1) Å). The thiocyanate group is bonded through its nitrogen atom (2.05(2) Å).

The nickel(II) complexes of a general formula  $\text{NiX}_2(\text{Htsc})_2$ , (Htsc means a molecule of thiosemicarbazide and  $\text{X} = \frac{1}{2} \text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{NO}_2^-$  or  $\text{ClO}_4^-$ ) are known in the crystalline form. All of them, except  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  and  $\text{Ni}(\text{NO}_2)_2(\text{Htsc})_2$ , are diamagnetic<sup>1-4</sup>.

It was supposed that the diamagnetic complexes of the mentioned type exhibit a square-planar coordination around Ni(II). This was actually proved by means of the X-ray structure analysis of some complexes<sup>5-7</sup>. The nickel(II) paramagnetic complexes of the type  $\text{NiX}_2(\text{Htsc})_2$  were most probably coordinated octahedrally, the  $\text{NCS}^-$  and  $\text{NO}_2^-$  groups, respectively, being bonded to the central atom through their nitrogen atoms<sup>2,4</sup>.

A systematic attention was paid<sup>5-10</sup> to the structures of complexes with the molar ratio  $\text{Ni(II)} : \text{Htsc} = 1 : 2$  or  $1 : 3$  but the crystal structure of a paramagnetic anhydrous complex of the type  $\text{NiX}_2(\text{Htsc})_2$  has not yet been solved. In particular the fact that the complex  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  exists in two modifications<sup>4</sup> attracted our attention. The green one, termed as the  $\alpha$ -modification, was prepared only in powder form whereas the  $\beta$ -modification crystallizes from its aqueous solution in light-blue crystals. Two modifications are also known to exist in the case of sulphate<sup>5,6</sup> and nitrate<sup>4,7</sup> with the molar ratio of  $\text{Ni(II)} : \text{Htsc} = 1 : 2$  as well as in the case of iodide<sup>4,11</sup> with the ratio of  $1 : 3$ .

## EXPERIMENTAL

### Unit Cell and Space Group

$\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  crystallizes in the monoclinic symmetry system. The space group determined from systematic extinctions on Weissenberg photographs is  $P 2_1/c$ . The approximate values of lattice constants were estimated from rotation and Weissenberg photographs and their refinement was carried out by means of the  $\text{Pb}(\text{NO}_3)_2$  calibrated Guinier powder photograph using copper  $K_\alpha$ -radiation. Two least-squares cycles (the program written by Lingvist and Wengelin<sup>12</sup>) yielded the following values:  $a = 5.300(4) \text{ \AA}$ ,  $b = 7.761(5) \text{ \AA}$ ,  $c = 16.12(2) \text{ \AA}$ ,  $\beta = 92.01(6)^\circ$ ; unit cell volume is  $662.56 \text{ \AA}^3$ . The density determined by the flotation method is  $1.77 \text{ g/cm}^3$ , the calculated value for two formula units in the unit cell is  $1.769 \text{ g/cm}^3$ .

### Intensity Data

Single crystals of  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  were prepared according to ref.<sup>2</sup>. They appeared in a needle-like form of a light-blue color. The Weissenberg and precession photographs were then prepared from 0.13 mm thick crystal using copper  $K_\alpha$ -radiation and taking three reciprocal lattice levels perpendicular to [100] and two levels perpendicular to [010]. The blackening of the diffraction spots was measured photometrically. The intensities of 590 independent reflections obtained in this way were then corrected for Lorentz and polarization factor as well as for  $\alpha_1$ ,  $\alpha_2$  splitting. The influence of an absorption was neglected ( $\mu R = 0.99$ ).

### Structure Analysis

The nickel atom occupies a centrosymmetric special position at the origin of the space group  $P 2_1/c$ . The remaining atoms are located in four-fold general positions<sup>13</sup>. The positions of heavier atoms were determined from the three-dimensional Patterson function; the coordinates of other atoms were found from electron-density maps.

The refinement of the atomic coordinates and the isotropic temperature factors as well as the scale factors was carried out by the least-squares method the function  $R' = \sum W(|F| - |F|)^2$  being minimized with block-diagonal approximation, using the Cruickshank's weighting scheme<sup>14</sup>. The atomic scattering factors used in the computing were those published by Ibers<sup>15</sup>. The final  $R$ -factor calculated upon  $|F|$  was 0.13 for observed reflections. The unobserved reflections were not used in the refinement. The maximum value of the electron density in the final difference synthesis did not exceed  $1.4 \text{ e/\AA}^3$ .

The final atomic coordinates together with the thermal coefficients are given in Table I.\* The observed and calculated values of the structure factors are available at authors.

### Description of Structure and Discussion

Bivalent nickel exhibits a heterogeneous octahedral coordination in the crystals of  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$ . Four nitrogen atoms are bonded to the central atom, two from the NCS-groups and two from the thiosemicarbazide. The Ni—N bonds are 2.05 and 2.13  $\text{\AA}$ , respectively, (Figs 1 and 2, as well as Table II). The above bond lengths are very close to the data published in the literature<sup>5-10, 18-23</sup>.

\* The calculations were made on the ZRA-1 computer (corrections of intensities) using the programs<sup>16</sup> and on the Elliott 803 B computer using the programs written by Daly, Stephens, and Wheatley<sup>17</sup>. The programs for the above computers were kindly provided by Institut für Strukturforchung DAW, Berlin—Adlershof (ZRA-1) and by Monsanto Research, Zürich (Elliott 803 B).

In all structures with thiocyanate-groups coordinated to a nickel atom through their nitrogen atom<sup>19-23</sup>, the Ni—N bond lengths fall within the interval 1.99—2.12 Å. The length of the bond in this structure is 2.05 Å, whereas the sum of covalent radii of nickel(II) and nitrogen atoms according to Pauling<sup>24</sup> is 2.19 Å.

The homogeneous square-planar coordination is completed to a tetragonal bipyramidal coordination by two sulphur atoms belonging to the thiosemicarbazide molecules with a Ni—S bond length of 2.45 Å. Two thiosemicarbazide molecules are coordinated to the nickel atom in a *trans*-configuration the central atom being at a center of symmetry; this leads to two five-membered approximately planar rings. The equation of the ring plane (in Å) is

$$0.6058X - 0.6677Y + 0.4326Z = 0.0221.$$

TABLE I

Final Atomic Coordinates (standard errors  $\times 10^3$  are given in parentheses) and Isotropic Temperature Coefficients

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>i</sub></i>
Ni	0.000	0.000	0.000	2.37
S 1	0.764 (1)	0.024 (1)	0.128 (0.3)	1.48
S 2	0.543 (1)	0.565 (1)	0.126 (0.3)	2.04
N 1	0.233 (4)	0.796 (2)	0.048 (1)	1.97
N 2	0.142 (4)	0.261 (2)	0.126 (1)	1.63
N 3	0.230 (4)	0.188 (2)	0.051 (1)	1.85
N 4	0.879 (5)	0.256 (3)	0.239 (1)	2.57
C 1	0.351 (5)	0.697 (3)	0.081 (1)	1.48
C 2	0.931 (5)	0.190 (2)	0.162 (1)	1.14

TABLE II

Bond Lengths in Ni(NCS)<sub>2</sub>(Htsc)<sub>2</sub> in Å (standard deviations  $\times 10^2$  are given in parentheses) (Figs 1, 2)

Atoms	Distance	Atoms	Distance
Ni—N'1	2.05 (2)	N'1—C'1	1.11 (3)
Ni—N 3	2.13 (2)	C'1—S'2	1.60 (2)
Ni—S 1	2.45 (1)	N 2—S 2	3.18 (2)
S 1—C 2	1.65 (2)	N 4—S 2	3.47 (2)
C 2—N 2	1.39 (3)	N 4—S''1	3.50 (2)
C 2—N 4	1.37 (3)	N 4—C'''1	3.23 (3)
N 2—N 3	1.44 (2)		

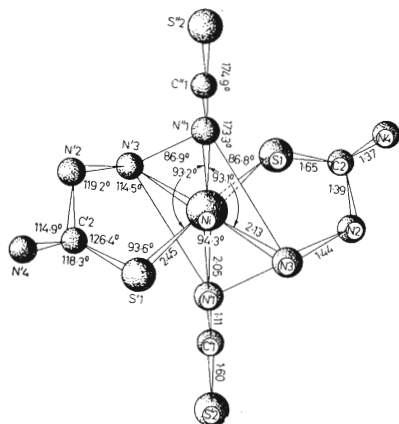


FIG. 1

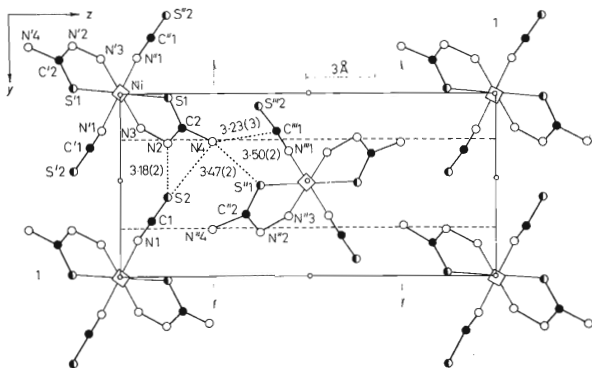
A Perspective Drawing of the  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  Molecule

FIG. 2

Packing of the  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  viewed along  $x$  Axis

TABLE III  
Bond Angles of Ni(NCS)<sub>2</sub>(Htcs)<sub>2</sub> in deg. (standard deviations × 10 in parentheses) (Figs 1, 2)

Atoms	Angle	Atoms	Angle
S 1-Ni-N 3	85.7 (5)	N 2-C 2-N 4	114.9 (18)
S 1-Ni-N' 3	94.3 (5)	C 2-N 2-N 3	119.2 (16)
S 1-Ni-N'' 1	86.8 (5)	N 2-N 3-Ni	114.5 (14)
S 1-Ni-N' 1	93.2 (5)	Ni -N' 1-C' 1	173.3 (17)
N' 3-Ni-N'' 1	86.9 (7)	N' 1-C' 1-S' 2	174.9 (24)
N 3-Ni-N'' 1	93.1 (7)	N 3-N 2-S 2	93.1 (12)
N 3-Ni-N' 3	180.0 (0)	C 2-N 2-S 2	147.3 (12)
Ni -S 1-C 2	93.6 (7)	C 2-N 4-C''' 1	148.7 (15)
S 1-C 2-N 2	126.4 (14)	S'' 1-N 4-C''' 1	116.1 (8)
S 1-C 2-N 4	118.3 (17)		

The deviations of individual atoms from this plane are the following (in Å): Ni -0.022; S<sub>1</sub> -0.038; C<sub>2</sub> -0.048; N<sub>4</sub> -0.017; N<sub>2</sub> -0.037, and N<sub>3</sub> +0.098.

The angles in the octahedron are approximately 90° (Table III). The angle N<sub>3</sub>-Ni-S<sub>1</sub> is the smallest with a value of 85.7°. This deformation is probably caused by strain in the five-membered ring and thus can be considered as a consequence of the chelate formation by the thiosemicarbazide molecules. The interatomic distances in a coordinated thiosemicarbazide as well as those in the NCS-group (Table II) are close to the corresponding values found in other structures.

In analyzing the results of both X-ray structural and other physico-chemical investigations it is possible to make some generalizations concerning the chemical and structural properties of the thiosemicarbazide ligand. It is known to be bonded in solid state complexes in any of three ways. The first one in which thiosemicarbazide is bonded only through its sulphur atom, the second one in which bonding through the sulphur atom and the nitrogen atom occur and the ligand acts as forming bridges, and the third one when thiosemicarbazide is a bidentate chelate ligand bonded through the sulphur atom and the nitrogen atom of the hydrazine group.

Whereas in the compounds with the molar ratio of Me : Htsc = 1 : 1 the thiosemicarbazide molecule can be bonded to the central atom either in the first<sup>25</sup> or in the second<sup>26</sup> or in the third<sup>27,28</sup> of the above mentioned ways, in the complex compounds with the molar ratio of Me : Htsc = 1 : 2 only chelate bonding of the thiosemicarbazide molecule was observed<sup>5-8,10</sup>. Our results give support to the above conclusions. The chelate formation was confirmed<sup>9</sup> also for complexes with a molar ratio of Me : Htsc = 1 : 3.

Systematic structural investigations of nickel(II) complexes with thiosemicarbazide as a ligand has been carried out<sup>5-10</sup> and in particular Grønbaek Hazell's results<sup>5-9</sup> make it possible to generalize the bonding description of the inner sphere in the above complexes.

A lengthening of the Ni—N distance was observed in the planar *cis*-isomer compared with the planar *trans*-isomer. This can be readily explained by a mutual influencing of ligands and in the given case by a labilization of the Ni—N bond caused by the sulphur atom in the *trans* position. Simultaneously a stabilization of the Ni—S bond takes place which results in its shortening. The Ni—S interatomic distances in both configurations are shorter than the sum of the corresponding covalent radii ( $1.15 + 1.04 \text{ \AA}$ ) and the Ni—N interatomic distances are longer than the sum of covalent radii<sup>6</sup> ( $1.15 + 0.74 \text{ \AA}$ ). The metal—ligand bonds in the planar Ni(II) complexes can be thus considered as a dynamical system, *i.e.* the lengthening of the Ni—N bonds causes the shortening of the Ni—S bonds. The sum of the interatomic distances Ni—S + Ni—N, however, is constant and its value is very close to the sum of covalent radii.

The interatomic distances in the crystal structure of  $\text{Ni}(\text{NCS})_2(\text{Htsc})_2$  are very close to those that have been found<sup>8</sup> in the pseudo-octahedral complex  $[\text{Ni}(\text{Htsc})_2 \cdot (\text{H}_2\text{O})_2](\text{NO}_3)_2$  which also exhibits the *trans* configuration of the thiosemicarbazide molecules. If the planar coordination is completed to the octahedral one an increase of the interatomic distances in the square-planar base was found. The strengthening of bonds in the square-planar complexes, if compared with bonds in the square-planar base of the pseudo-octahedral complexes, is probably due to the contribution of *d*-orbitals of the nickel atom to the formation of metal—ligand  $\pi$ -bonds.

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