The four coordinating nitrogens and the nickel ion are almost coplanar, with deviations less than 0·02 Å and, as the angles N—Ni—N deviate by less than 0·2° from the ideal value, the square-planar geometry is almost perfect. The average Ni—N bond length of 1·86 (1) Å indicates that the compound is a low-spin complex (see *e.g.* Ito & Toriumi, 1981; Madaule-Aubry, Busing & Brown, 1968). The overall geometry of the complex resembles that of anionic bis(biuretato)-metal complexes. In these complexes the biuret molecules act as bidentate ligands through their deprotonated amide nitrogen atoms (see *e.g.* Birker, Freeman, Guss & Watson, 1977; Siegel & Martin, 1982, and references therein).

The structure is held together by *inter alia* an extensive net of hydrogen bonds. Thus, the imino nitrogens N(1), N(3), N(1′) and N(3′) participate as donors in hydrogen bonds to the chlorine atom Cl(1), [N···Cl ranging from 3·351 (4) to 3·414 (4) Å]. The amino nitrogens N(2) and N(2′) form hydrogen bonds to two water molecules O(*w*2) and O(*w*1) [N···O distances 2·746 (6) and 2·734 (6) Å respectively]. Other hydrogen bonds occur between the water molecules [O···O from 2·686 (6) to 2·759 (6) Å] and between the chlorine atoms and the water molecules [O···Cl from 3·125 (4) to 3·201 (4) Å].

The square-planar complexes are stacked along the **a** direction (Fig. 2) but with the molecular planes inclined in such a way that the complexes are parallel to the $(10\bar{1})$ planes, yielding a very strong $20\bar{2}$ reflexion. The chlorine atoms and the water molecules occupy the space between the molecular stacks.

The author is indebted to Dr I. Crossland, Department of Organic Chemistry, The Technical University of Denmark, for his generous supply of acetamidine and for stimulating discussions.

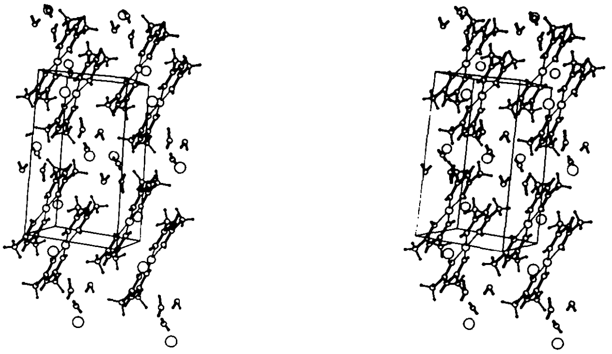

Fig. 2. Packing diagram of the crystal structure with *c* vertical, *a* horizontal and *b* out of the plane of the paper. The larger circles represent the chlorine atoms.

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Structure of Bis(isothiocyanato)tetrakis(pyridine)nickel(II), $C_{22}H_{20}N_6NiS_2$, a Redetermination

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(*Received* 25 *July* 1983; *accepted* 28 *February* 1984)

Abstract. $M_r = 491{\cdot}28$, monoclinic, $C2/c$, $a = 12{\cdot}434\ (4)$, $b = 12{\cdot}944\ (5)$, $c = 16{\cdot}461\ (6)$ Å, $\beta = 118{\cdot}78\ (2)°$, $V = 2322{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}39$, $D_x = 1{\cdot}41$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}03$ mm^{-1}, $F(000) = 1016$, $T = 298$ K. Final $R = 0{\cdot}063$ for 1300 observed reflections. The structure consists of close-packed units. The Ni$^{\rm II}$ atoms are pseudo-octahedrally *trans*-coordinated by two N atoms

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

For non-H atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B
Ni	0	0	0	2·93 (4)
S(1)	0·4041 (1)	0·1066 (1)	0·0812 (1)	5·00 (7)
N(1)	0·1549 (4)	0·0773 (3)	0·0177 (3)	3·8 (2)
N(2)	0·1032 (4)	−0·0603 (3)	0·1398 (3)	3·5 (2)
N(3)	−0·0511 (4)	0·1271 (3)	0·0586 (3)	3·7 (2)
C(1)	0·2578 (5)	0·0894 (4)	0·0442 (3)	3·3 (2)
C(2)	0·0735 (5)	−0·1498 (5)	0·1646 (4)	4·4 (2)
C(3)	0·1394 (6)	−0·1919 (5)	0·2515 (4)	5·3 (3)
C(4)	0·2401 (6)	−0·1407 (5)	0·3184 (4)	6·0 (3)
C(5)	0·2709 (6)	−0·0495 (6)	0·2934 (4)	5·7 (3)
C(6)	0·2019 (5)	−0·0096 (4)	0·2047 (4)	4·4 (2)
C(7)	−0·1117 (5)	0·1112 (5)	0·1073 (4)	4·9 (3)
C(8)	−0·1490 (6)	0·1916 (5)	0·1432 (4)	5·8 (3)
C(9)	−0·1280 (6)	0·2917 (5)	0·1279 (5)	6·1 (3)
C(10)	−0·0656 (6)	0·3073 (5)	0·0777 (5)	5·8 (3)
C(11)	−0·0316 (5)	0·2248 (4)	0·0451 (4)	4·6 (3)
H(1)	0·003 (4)	−0·180 (4)	0·118 (4)	2 (1)
H(2)	0·118 (5)	−0·250 (4)	0·266 (3)	2 (1)
H(3)	0·293 (6)	−0·174 (5)	0·379 (5)	8 (2)
H(4)	0·338 (7)	−0·006 (4)	0·334 (5)	4 (2)
H(5)	0·221 (5)	0·054 (4)	0·187 (4)	3 (1)
H(6)	−0·132 (5)	0·051 (5)	0·116 (4)	4 (2)
H(7)	−0·198 (6)	0·174 (4)	0·176 (4)	4 (1)
H(8)	−0·138 (5)	0·357 (4)	0·148 (4)	4 (1)
H(9)	−0·055 (5)	0·375 (4)	0·071 (4)	5 (2)
H(10)	0·024 (5)	0·231 (4)	0·017 (4)	2 (1)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ni–N(1)	2·062 (8)	C(2)–C(3)	1·37 (2)
Ni–N(2)	2·169 (31)	C(3)–C(4)	1·38 (2)
Ni–N(3)	2·151 (8)	C(4)–C(5)	1·36 (1)
S(1)–C(1)	1·63 (2)	C(5)–C(6)	1·39 (2)
N(1)–C(1)	1·15 (1)	C(7)–C(8)	1·38 (1)
N(2)–C(2)	1·339 (8)	C(8)–C(9)	1·37 (1)
N(2)–C(6)	1·35 (2)	C(9)–C(10)	1·39 (2)
N(3)–C(7)	1·36 (1)	C(10)–C(11)	1·35 (1)
N(3)–C(11)	1·327 (7)		
N(1)–Ni–N(2)	89·4 (2)	N(2)–C(2)–C(3)	123·2 (5)
N(1)–Ni–N(3)	91·3 (2)	C(2)–C(3)–C(4)	120·0 (6)
N(2)–Ni–N(3)	92·8 (2)	C(3)–C(4)–C(5)	117·1 (6)
Ni–N(1)–C(1)	156·2 (4)	C(4)–C(5)–C(6)	121·3 (5)
Ni–N(2)–C(2)	121·7 (3)	N(2)–C(6)–C(5)	121·1 (6)
Ni–N(2)–C(6)	120·9 (4)	N(3)–C(7)–C(8)	122·3 (6)
C(2)–N(2)–C(6)	117·4 (4)	C(7)–C(8)–C(9)	120·1 (8)
Ni–N(3)–C(7)	121·1 (4)	C(8)–C(9)–C(10)	117·1 (7)
Ni–N(3)–C(11)	122·5 (5)	C(9)–C(10)–C(11)	119·5 (6)
C(7)–N(3)–C(11)	116·3 (6)	N(3)–C(11)–C(10)	124·7 (7)
S(1)–C(1)–N(1)	180 (1)		

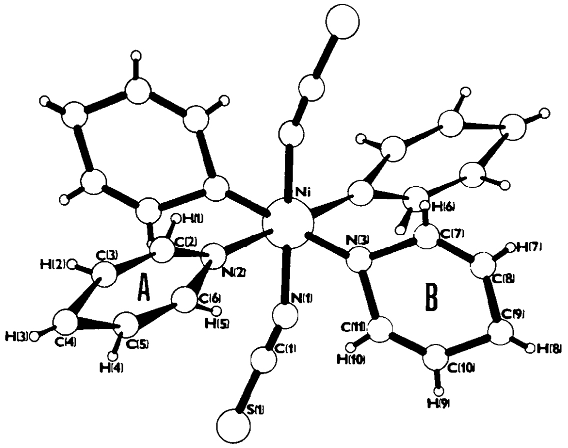

Fig. 1. Structure of the $[Ni(NCS)_2(py)_4]$ complex.

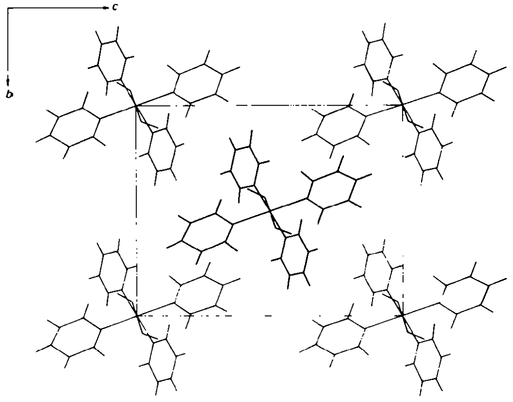

Fig. 2. Projection of the crystal structure on (100).

from monodentate NCS groups and by four N atoms from the pyridine rings with a coordination number of $2 + 4$. The N—C—S bond angle is 180 (1)° and the distances N—C and C—S are 1·15 (1) and 1·63 (2) Å. The pyridine rings are almost planar.

Introduction. In the series of thiocyanatonickel(II) complexes, $[Ni(NCS)_2(py)_4]$ (py = pyridine) is of great importance in studies of the characteristics of the NCS group. In an incomplete model of the crystal structure of this compound determined from projection data (Poraj-Košic & Antzishkina, 1958) Ni^{II} is pseudo-octahedrally *trans*-coordinated similarly to the complexes $Ni(py)_4X_2$, $X = Br$, and $Ni(NH_3)_4X_2$, $X = NO_2$, NCS (Poraj-Košic, Antzishkina, Dikareva & Jukhnov, 1957). For a more exact comparison of the title complex with other Ni^{II} complexes, from the aspect of the geometry of the coordination polyhedron (Gažo *et al.*, 1982), the redetermination and refinement of this crystal structure was carried out.

Experimental. Dark-blue prism-shaped crystals prepared as already described (Grossmann & Hünseller, 1905); D_m measured by flotation; Weissenberg photographs indicated space group *Cc* or *C*2/*c*; cell parameters refined on Syntex $P2_1$ computer-controlled four-circle diffractometer with graphite-monochromated Mo *K*α radiation by least squares from the angles of ten selected reflections; intensity measurements carried out within $0 \leq 2\theta \leq 55°$ using θ–2θ scans with a variable scan speed ranging from 4·88 to

29·3° min^{-1}; scan range 2θ(Mo $K\alpha_1$)−1° to 2θ(Mo $K\alpha_2$)+1°; two standard reflections remeasured after every 98 reflections, intensity variation $< 3\%$; 2479 reflections measured, 1300 [$I > 1{\cdot}96\,\sigma(I)$] used in analysis, *hkl* range 0/14, 0/16, −19/18; intensities corrected for Lorentz–polarization effects; empirical absorption corrections (ψ scans) applied (min. transmission factor 0·71, taking max. transmission as unity); heavy atom located from the three-dimensional Patterson function, centrosymmetric space group *C*2/*c* selected; remaining non-H atoms located by difference Fourier synthesis; structure refined by least squares on *F* using a block-diagonal approximation with anisotropic temperature coefficients; H atoms placed in calculated positions and refined; $w = 1/\sigma^2(F)$, final $R = 0{\cdot}063$, $R_w = 0{\cdot}087$, $S = 0{\cdot}036$; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·265; max. and min. values of residual $\Delta\rho$ 0·3 and −0·4 e Å^{-3}; scattering factors from Cromer & Waber (1965). All calculations carried out with *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. Final atomic parameters are in Table 1.*

The structure consists of discrete units of $Ni(NCS)_2(py)_4$ which are mutually held together by van der Waals forces. The Ni atoms occupy centrosymmetric positions; the Ni atom, as shown in Fig. 1, is coordinated by four N atoms from the pyridine rings and by two N atoms from the monodentate NCS groups. Bond distances and angles are listed in Table 2. The projection of the structure is pictured in Fig. 2.

Mean values of the Ni—N bond distances in the equatorial plane and in the axial direction of the slightly compressed octahedral coordination geometry are 2·16 and 2·06 Å respectively, and correspond to the values in Ni^{II} complexes with chromophores NiN_6 and *trans*-NiN_4O_2 (Jóna, Valach, Gažo, Fendrich & Šramko, 1983). The Ni—N(2), 2·17 (3) Å, and Ni—N(3), 2·151 (8) Å, bond lengths are close to the length of Ni—N(py), 2·148 (9) Å, in the $Ni(NCS)_2(pip)_2(py)(H_2O).2(pip)$ (pip is piperidine) structure (Koman, Ďurčanská, Handlovič & Gažo, 1983). The NCS groups are linear. The N(1)—C(1), 1·15 (1) Å, and C(1)—S(1), 1·63 (2) Å, lengths correspond to triple and single bonds (*International Tables for X-ray Crystallography,* 1962).

Both pyridine rings (*A* and *B* in Fig. 1) are almost planar, $\chi^2_A = 1{\cdot}6$, $\chi^2_B = 4{\cdot}2$, and their least-squares planes make dihedral angles of 114·8 (3) and 56·8 (3)° with the equatorial NiN_4 [Ni, N(2), N(3), N(2′), N(3′)] plane; the inter-ring angle is 101·9 (3)°. Deviations of atoms from the least-squares planes of both pyridine rings have been deposited.* The bond lengths N—C, 1·340 Å, and C—C, 1·390 and 1·400 Å, in the molecule of pyridine in the gas phase (Bak, Hansen & Rastrup-Andersen, 1954) are in good agreement with the mean N—C and C—C values: 1·34 (2), 1·37 (2) Å in ring *A* and 1·341 (8), 1·374 (7) Å in ring *B*. Bond angles in the pyridine molecule are C—N—C 116·70, N—C—C 124·00, C—C—C 118·60 and 118·10° (Bak *et al.*, 1954); the mean values of these angles in ring *A* are 117·4 (4), 122·2 (4) and 119·4 (3)° and in ring *B* 116·3 (6), 123·5 (5) and 118·9 (4)°.

The authors are indebted to Dr E. Jóna of the Slovak Technical University, Bratislava, for the preparation of the crystals.

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* Lists of structure factors, anisotropic thermal parameters, parameters of least-squares planes and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39271 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.