Structural investigations of nickel(II) complexes II.* Crystal and molecular structure of diisothiocyanate-bis(2,5-dimethylpyridine)nickel(II) complex

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The title compound, $Ni(NCS)_2(2,5\text{-diMepy})_2$, crystallizes in monoclinic system: space group $P2_1/c$, two molecules per unit cell of $a = 8.785(3)$, $b = 5.279(3)$, $c = 19.603(20) \times 10^{-10}$ m, and $\beta = 93.28(5)°$ dimensions. The crystal structure was solved using the heavy-atom method and refined by the method of full matrix least squares leading to the final R value of 0.062. The central atom of the molecular complex was located at the centre of symmetry and it was surrounded in an approximately square-planar arrangement by four nitrogen atoms of the ligands at Ni—N distances of 1.865 (NCS group) and 1.910×10^{-10} m (2,5-diMepy), respectively. $Ni(NCS)_2(2,5\text{-diMepy})_2$ molecules were held together by contacts of S atoms with dimethylpyridine rings of the neighbouring complex molecules.

Исследуемое соединение $Ni(NCS)_2(2,5\text{-diMepy})_2$ кристаллизируется в моноклинической сингонии: пространственная группа $P2_1/c$, две молекулы в элементарной ячейке с размерами $a = 8,785(3)$, $b = 5,279(3)$, $c = = 19,603(20) \cdot 10^{-10}$ м, и $\beta = 93,28(5)°$. Кристаллическая структура определена методом тяжелого атома и уточнена методом наименьших квадратов до значения $R = 0,062$. Центральный атом молекулярного комплекса локализован в центре симметрии и окружен четырьмя атомами азота от лигандов с расстоянием Ni—N (10^{-10} м) 1,865 (NCS группа) и 1,910 (2,5-diMepy), с образованием квадратного координационного полиэдра Ni. Межмолекулярные контакты молекул $Ni(NCS)_2(2,5\text{-diMepy})_2$ осуществляются атомами S с циклами диметилпиридина соседних молекул.

The complex of $Ni(NCS)_2(2,5\text{-dimethylpyridine})_2$ belongs to a group of compounds of $Ni(NCS)_2(\text{alkylpyridine})_2$ in which at least one alkyl substituent is

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* For Part I see Ref. [8].

situated in the 2-position to the nitrogen atom of the organic ligand. These complexes were investigated by means of electron absorption spectra as well as by magnetic measurements [1] and they were found to have a square-planar configuration. The title compound is the first of them with studied crystal and molecular structure. The structural study of this compound should inform of the influence of 2-methyl substituted pyridine on the planar coordination of nickel(II) atom as well as the bonding type of the NCS group as pseudohalogenide ligand with respect to the mutual influence of ligands.

Experimental

$Ni(NCS)_2(2,5$-dimethylpyridine$)_2$ was prepared [2] as follows: the powdered $Ni(NCS)_2$ (1.75 g; 0.01 mol) was dissolved in toluene (20 cm^3) at 60°C: the solution was filtrated off and mixed with 2,5-dimethylpyridine (2.14 g; 0.02 mol). Crystals suitable for X-ray diffraction experiment were obtained by slow evaporation of the solution at 60°C. The red needle-shaped crystals were elongated parallel to b. Crystal data are reported in Table 1.

Table 1

Crystal data for $Ni(NCS)_2(2,5$-diMepy$)_2$

Formula		$NiN_4S_2C_{16}H_{18}$
M		389.19
Cell dimensions	a	$8.785(3) \times 10^{-10}$ m
	b	5.279(3)
	c	19.603(20)
	β	93.28(5)°
	V_c	907.6×10^{-30} m^3
D_m		1.42 g cm^{-3}
D_c		1.42 g cm^{-3}
Z		2
Space group		$P2_1/c$ (No. 14)
$F(000)$		404
$\mu(MoK_\alpha)$		12.9 cm^{-1}

Unit cell dimensions were determined using least squares procedures on the angular positions of 10 reflections centred on Syntex $P2_1$ automatic diffractometer. Intensity data were collected according to Table 2. The intensities of reflections were corrected for Lorentz and polarization factors. Since the used crystal was of approximate dimensions of $0.03 \times \times 0.02 \times 0.05$ cm (Table 2), no absorption correction was made.

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Table 2

Conditions of intensity data collection

Radiation	$\text{Mo}K_\alpha$ ($\lambda = 0.71069 \times 10^{-10}$ m)
Monochromator	Graphite
Crystal dimensions, cm	0.03, 0.02, 0.05
Scan mode	$\Theta : 2\Theta$
Scan speed, °/min	4.88—29.3
Scan range	$\pm 1°$ from the peak centre
Background count	0.5 of the reflection scan time at each end of the scan
Check reflections	2 every 98 reflections; no decay
Data collection limits	$0 < 2\Theta < 55°$
	$h, k, \pm l$
Number of data collected	2015
Number of data with $I > 1.96\ \sigma(I)$	938

Structure determination and refinement

The coordinates of nickel and sulfur heavy atoms were determined from a Patterson synthesis and all other nonhydrogen atoms were located from a Fourier electron density synthesis phased on the position of heavy atoms. The atom parameters were refined by full matrix least squares method. After three cycles of istropic and three cycles of anisotropic refinement, two hydrogen atoms of both methyl groups were located by difference Fourier synthesis and remaining H atom positions were determined considering the hybridization of C atoms with C—H distance of 0.95×10^{-10} m. Further refinement included parameters of the positions of hydrogen atoms, the temperature factors assigned to the hydrogen atoms being isotropic. The final values of R were $R_1 = 0.086$ defined as $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_2 = 0.062$ ($R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w = 1/\sigma_F^2$ and $\sigma_F = [(F_o - \sigma_I/L_p)^{1/2} - F_o]$) for 938 observed reflections (with $I \geqslant 1.96\ \sigma_I$). The positional and thermal parameters of the atoms with their estimated standard deviations are listed in Tables 3 and 4. The interatomic distances and bond angles with their standard deviations are given in Table 5 and shown in Fig. 1. Packing of the molecules in the unit cell is shown in Fig. 2.

All programs used during the solution of the structure and its refinement were from an XTL program system supplied by Syntex Corporation.

Structure description and discussion

The complex of $\text{Ni(NCS)}_2\text{(2,5-diMepy)}_2$ had a monomeric structure with centrosymmetric arrangement of ligands showing a slightly distorted square-planar configuration with four nitrogen atoms in coordination sphere. The Ni—N(1) and Ni—N(2) distances were 1.865(8) and $1.910(7) \times 10^{-10}$ m, respectively (Table 5), corresponding to those in other square-planar Ni(II) complexes [3—6].

Fractional coordinates of atoms ($\cdot 10^4$) with *esd*'s in parentheses

Atom	x	y	z
Ni	0	0	0
S	−2959(3(	−4535(6)	1433(1)
N(1)	−1138(9)	−1882(16)	595(4)
N(2)	1468(9)	740(14)	724(3)
C(1)	−1919(11)	−2969(19)	940(5)
C(2)	2861(11)	− 306(23)	788(4)
C(3)	3912(13)	573(21)	1299(5)
C(4)	3471(13)	2375(24)	1755(6)
C(5)	2036(15)	3387(20)	1707(5)
C(6)	1030(13)	2497(21)	1194(5)
C(7)	3278(14)	−2232(27)	290(6)
C(8)	1463(19)	5366(29)	2199(7)

Fractional coordinates ($\cdot 10^2$) for the hydrogen atoms

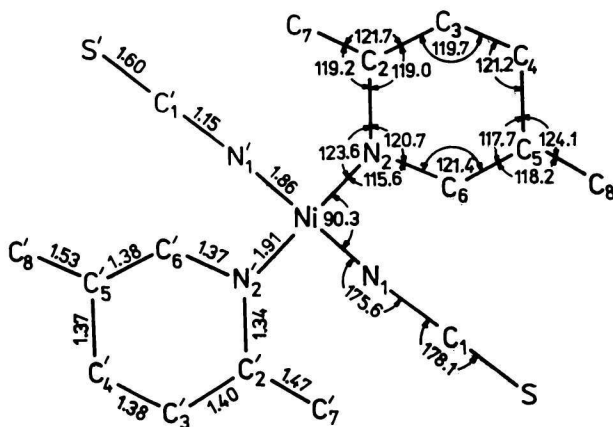| Atom	x	y	z
H C3'	50	45	13
H C4	45	30	20
H C6	0	32	12
H1 C7	39	64	48
H2 C7	34	−37	0
H3 C7	24	72	1
H1 C8	15	52	26
H2 C8	3	61	20
H3 C8	23	66	22

Fig. 1. Bond lengths (10^{-10} m) and angles (°) in the molecule.

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Table 4

Anisotropic thermal parameters (10^{-22} m^2) with *esd*'s in parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	423(11)	272(8)	277(8)	−17(12)	17(8)	25(10)
S	566(19)	479(19)	509(15)	−27(17)	197(14)	87(15)
N(1)	406(56)	419(49)	451(48)	−55(44)	98(41)	51(42)
N(2)	415(17)	277(46)	296(35)	−25(36)	22(34)	20(35)
C(1)	346(56)	315(52)	302(46)	83(48)	67(45)	−78(44)
C(2)	262(46)	375(57)	327(43)	24(56)	39(38)	126(53)
C(3)	441(60)	430(73)	476(52)	145(55)	104(49)	−15(52)
C(4)	307(62)	513(70)	545(65)	−60(55)	56(52)	51(55)
C(5)	682(78)	313(54)	230(45)	−66(56)	122(51)	−15(44)
C(6)	526(68)	334(58)	325(48)	17(54)	26(53)	73(45)
C(7)	447(71)	554(78)	480(64)	101(67)	123(57)	−158(59)
C(8)	956(99)	473(82)	416(56)	−74(86)	54(68)	−1(83)

Thermal parameters are in the form

$$\exp\left[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

The isotropic temperature factors of hydrogen atoms were taken as 6.0×10^{-20} m^2.

Interatomic distances and angles, with *esd*'s in parentheses

Atoms	Distance/10^{-10} m	Atoms	Distance/10^{-10} m
Ni—N(1)	1.865(8)	C(4)—H	0.976(93)
Ni—N(2)	1.910(7)	C(6)—H	0.976(92)
N(1)—C(1)	1.145(13)	C(7)—H(1)	1.141(89)
C(1)—S	1.598(10)	C(7)—H(2)	0.950(13)
N(2)—C(2)	1.342(15)	C(7)—H(3)	0.851(98)
C(2)—C(3)	1.403(14)	C(8)—H(1)	0.853(37)
C(3)—C(4)	1.376(16)	C(8)—H(2)	1.088(95)
C(4)—C(5)	1.367(17)	C(8)—H(3)	0.950(16)
C(5)—C(6)	1.383(15)		
C(6)—N(2)	1.371(13)	S...H(C4)	2.878(94)
C(2)—C(7)	1.470(17)	S...H(C6)	2.919(91)
C(5)—C(8)	1.526(18)		
C(3)—H	1.087(86)	S...H2(C8)	3.093(94)

Bonds	Angles/°	Bonds	Angles/°
N(1)—Ni—N(2)	90.26(33)	C(7)—C(2)—C(3)	121.67(97)
Ni—N(1)—C(1)	175.62(32)	C(2)—C(3)—C(4)	119.66(101)
N(1)—C(1)—S	178.07(94)	C(3)—C(4)—C(5)	121.21(103)
Ni—N(2)—C(2)	123.64(64)	C(4)—C(5)—C(8)	124.05(109)
Ni—N(2)—C(6)	115.62(64)	C(8)—C(5)—C(6)	118.18(105)
C(2)—N(2)—C(6)	120.72(83)	C(4)—C(5)—C(6)	117.74(103)
N(2)—C(2)—C(3)	119.02(91)	C(5)—C(6)—N(2)	121.43(96)
N(2)—C(2)—C(7).	119.21(92)		

The pyridine rings lay in planes (deviations of atoms from the plane are given in Table 6) forming with the coordination plane a dihedral angle of 74.63°.

This orientation of 2-substituted pyridine ligands caused the location of 2-methyl substituents in the regions of possible fifth and sixth coordination places (axial interactions) of Ni atom (the Ni...C(7) distance being 3.15×10^{-10} m) and consequently the stabilization of square-planar geometry of the coordination sphere in conditions of its formation. Stoichiometrically similar compounds, containing 2,6-disubstituted pyridines were described [7] as unique complexes among the many known Ni(II)-pyridine derivatives because of their lack of solubility and chemical reactivity. This behaviour of 2,6-disubstituted ("doubly hindered") pyridine complexes is especially striking if compared with $Ni(NCS)_2L_2$ complexes if L is "monohindered" pyridine ligand (one of two 2-positions of pyridine ligands is alkyl-substituted), *e.g.* with the compound under investigation.
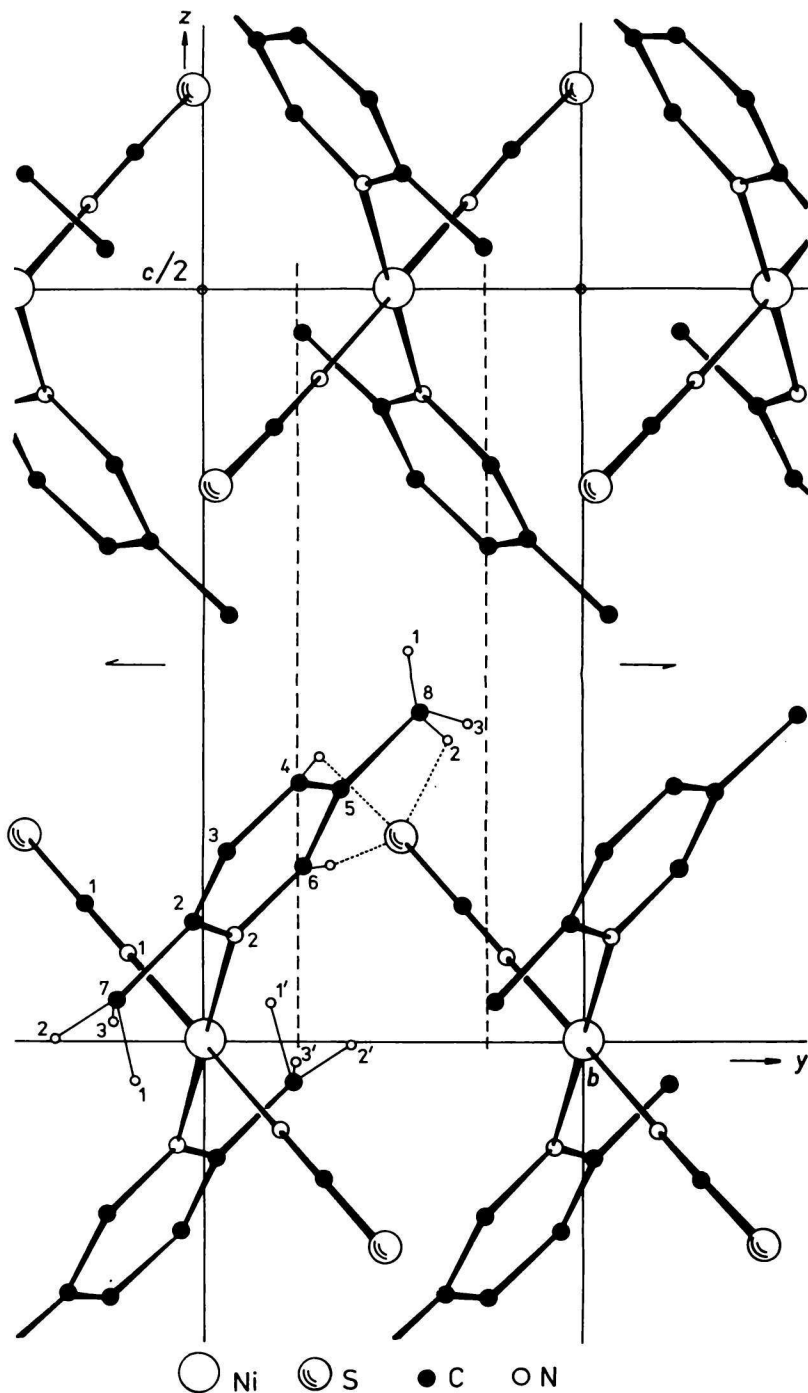
Fig. 2. Packing of the molecules. Projection along the *a* axis.

◯ Ni ◎ S ● C ○ N

Table 6
Deviations of atoms from the plane *I**

Atom	Deviation/10^{-14} m
N(2)	152(72)
C(2)	−237(105)
C(3)	104(103)
C(4)	25(121)
C(5)	24(105)
C(6)	−193(103)
C(7)	−196(132)
C(8)	−223(152)

* The equation of the plane *I* passing through N(2), C(2), C(3), C(4), C(5), and C(6) is

$$0.3503\ X + 0.7178\ Y - 0.6017\ Z + 0.17 = 0.$$

The equation of the plane *II* passing through Ni, N(1), and N(2) is

$$0.5254\ X - 0.3219\ Y - 0.2200\ Z - 0.0 = 0.$$

The angle of the planes *I* and *II* is 105.37°.

This one is soluble in organic solvents and it is also instantly decomposed by water and by inorganic acids. The reactivity of "monohindered" pyridine complexes may be connected with the similar effect as that found in the compound $Ni(NCS)_2(quinoline)_2(H_2O)_2 \cdot 2quinoline$ [8] in which the quinoline rings (quinoline is sterically assumed as 2-substituted pyridine) lie on planes forming with the NiN_4 equatorial plane an angle of 47°. Such an orientation of quinoline ligands makes the axial positions of Ni(II) atom vacant for bonding of small ligands, as *e.g.* water molecules. The decomposition of 2,5-dimethylpyridine complex upon contacts with water might begin by changing the original pyridine-plane orientation to that making possible axial interactions, immediate bonding of water molecules initiating the hydrolysis of the complex. The crystalline $Ni(NCS)_2L_2$ complexes of doubly hindered pyridines may be taken as having analogical orientation of pyridine planes as in monohindered pyridine complexes, but with two pairs of CH_3 groups in both axial positions of the central atom. Their mutual hindrance does not allow the necessary deviation from their original positions and the axial positions of nickel atom become impenetrable for further ligand bonding.

The thiocyanate group is nearly linear, the N(1)—C(1)—S angle being 178.0° and is deviated from the direction of Ni—N(1) bond by 4.4° (Table 5). This deviation is significantly smaller than that found for pseudooctahedral Ni(II) complexes, *viz.* 25.7° for $Ni(NCS)_2(4\text{-methylpyridine})_4$ [9]; 23.3 and 16.5° for $Ni(NCS)_2(4\text{-methylpyridine})_4$ [10]; 26.26° for $Ni(NCS)_2(quinoline)_2(H_2O)_2 \cdot 2qui$-noline [8]. It is known that NCS group as ligand is able to form various bonding types and its bonding properties depend on its environment.

The actual terminal bonding mode of the NCS group as a pseudohalogenide ligand may be seen as a manifestation of mutual influence of ligands (understood as an interaction ligand—central atom—ligand). In the compounds $M(NCX)_2L_2$ the bonding mode of pseudohalogenide NCX groups can be influenced by the exchange of M, X or L, respectively (M = Ni or Cu, X = S or O, and L = py, 2,5-diMepy or 2,6-diMepy) and it is consequently connected with coordination geometry: the terminal bonding of the NCX groups leads to a square-planar configuration while the bridge-bonding yields a pseudooctahedral complex geometry. The bonding types of pseudohalogenide ligands caused by exchange of M, X or L are shown in Table 7.

Table 7

Complex geometry in the compounds $M(NCX)_2L_2$

M	X	L		
		py	2,5-diMepy	2,6-diMepy
Ni	S	po [11]	s [This paper]	s [7]
Cu	S	po [12]	po [13]	po [13]
Cu	O	po [14]	s [15]	s [15]

po — pseudooctahedral; s — square-planar.

It is evident that the bonding properties of pseudohalogenide ligands in the compounds $Ni(NCS)_2L_2$ are connected with further consequences: with stereochemical properties of the complex and also with the type of crystal structure (monomeric or polymeric).

Interatomic distances in dimethylpyridine ligands were quite regular (Table 5, Fig. 1) and agreed with those in other methylpyridine ligands. The bond angles on N(2) atom Ni—N(2)—C(2) of 123.6° and Ni—N(2)—C(6) of 115.6° (Table 5, Fig. 1) showed a deviation of the pyridine ring from the usual symmetrical position. It can be influenced by interaction of C(7) and C(8) methyl groups of adjacent molecules: the C(7)...C(8) distance is found to be 4.13×10^{-10} m which is near to the value of the sum of van der Waals radii of methyl groups (4.0×10^{-10} m) [16]. The contacts between molecules are consistent with van der Waals interactions, the three shortest of them are given in Table 5.

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