Structural investigations of nickel(II) complexes

IV. Preparation, properties, and crystal structure of $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$

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Complex compound $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$ crystallizes in monoclinic system with the space group $C\,2/c$. The unit cell dimensions are $a = 144.09$ pm, $b = 172.51$ pm, $c = 140.81$ pm, $\beta = 109.32°$, and $Z = 4$. The crystal structure was refined by the least-squares method anisotropically to $R = 8.5$ %.

The Ni(II) atom has a pseudooctahedral coordination of atoms $NiN_2N^1_2N^2O$ (N being the nitrogen atom from the NCS group, N^1 — from the piperidine ligand, N^2 — from the pyridine ligand, and O — oxygen atom from the coordinated water molecule) with the bond lengths Ni—N 20.64 pm, Ni—N^1 22.08 pm, Ni—N^2 21.48 pm, and Ni—O 21.65 pm. The two next piperidine molecules are bonded by hydrogen bonds with the water molecule. The bond length O...N (the nitrogen atom from the noncoordinated piperidine molecules) is 28.67 pm. The NCS groups are bonded terminally through the nitrogen atoms.

Комплексное соединение $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$ имеет следующие структурные характеристики: моноклинная сингония, пространственная группа $C\,2/c$, $a = 144{,}09$ пм, $b = 172{,}51$ пм, $c = 140{,}81$ пм, $\beta = 109{,}32°$ и $Z = 4$. Кристаллическая структура была уточнена анизотропно с помощью МНК до $R = 8{,}5$ %.

Атом Ni(II) обладает псевдооктаэдрической координационной сферой состава $NiN_2N^1_2N^2O$ (N — атом азота NCS-группы, N^1 — атом азота пиперидина, N^2 — атом азота пиридина, O — атом кислорода координированной воды). Длины связей равны: Ni—N = 20,64 пм, Ni—N^1 = 22,08 пм, Ni—N^2 = 21,48 пм, Ni—O = 21,65 пм. С молекулой воды водородными связями связаны две молекулы пиперидина. Длина связи O...N (атом азота некоординированной молекулы пиперидина) равна 28,67 пм. Группы NCS являются монодентатными и связаны через атом азота.

The *trans* influence of ligands is one of the manifestations of mutual influence of ligands. It is defined as a degree of central atom—ligand bond weakening caused by the ligand bonded in *trans* position [1, 2]. During the study of this phenomenon in

Ni(II) complexes stereochemical data for their structures with chromophores NiN_5X and NiN_4O_2, respectively, have been collected and the interatomic distances Ni—N and Ni—O have been studied. It was shown [3] that the interatomic distances Ni—O evidently depend on the interatomic distances $Ni—N_{trans}$ and $Ni—N_{cis}$. The pseudooctahedral complex *cis*-$[NiN_4O_2]$ represents the system, where the elongation of Ni—O bond causes the shortening of $Ni—N_{trans}$ bond and *vice versa* [3].

The complex compound $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$ (complex *I*) contains the chromophore $[NiN_2N^1_2N^2O]$ where N is the nitrogen atom from the NCS group, N^1 from the piperidine, N^2 from the pyridine, and O is the oxygen atom from the water molecule. The structure analysis results presented in this paper show that the interatomic distance Ni—N pyridine is influenced by the substitution of different ligands in *trans* position.

Experimental

Preparation of $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$ *and indirect structural methods results*

The crystals of complex *I* were prepared by recrystallization of $Ni(NCS)_2(pipe)_4$ from 10 % solution of piperidine in benzene [4]. The chemical analysis of prepared crystals led to the formula $Ni(NCS)_2(pipe)_5$ (the observed values: 9.33 % Ni, 15.69 % N, 52.64 % C, and 8.39 % H; the calculated values: 9.77 % Ni, 16.29 % N, 53.90 % C, and 9.20 % H). The X-ray structure analysis confirmed the formula corresponding to the complex *I* (the title complex). The presence of water in the complex *I* can be explained by recrystallization conditions: free evaporation of solution in air. The pyridine was probably present as an impurity in the piperidine used for recrystallization.

Electronic absorption spectra with two absorption maxima at $\tilde{\nu} = 15\,800\ cm^{-1}$ and $\tilde{\nu} = 25\,700\ cm^{-1}$ (Specord UV VIS 200, Zeiss, Jena) show that the Ni(II) atom is octahedrally coordinated. The position and the character of absorption maxima in the i.r. spectrum indicate the terminal bonding of the NCS groups through the nitrogen atoms: $\tilde{\nu}(CN) = 2080\ cm^{-1}$, $\tilde{\nu}(CS) = 810\ cm^{-1}$, $\tilde{\nu}(N—C—S) = 484\ cm^{-1}$ (measured by Specord 75 IR in nujol).

Complex *I* decomposes thermally in three steps: the decomposition starts at 60 °C — the loss 43 mass % corresponds to the release of two piperidine, one pyridine and one water molecules from one molecule of the complex. The second step of decomposition starts at 125 °C and the third one at 240 °C. The loss of mass at each of these steps corresponds to the release of one piperidine molecule from the complex.

Structure determination and refinement

The basic crystallographic data were determined from the oscillation and the Weissenberg photographs and refined using the positions of ten diffractions centred on Syntex $P2_1$ automatic diffractometer. They are summarized in Table 1.

Table 1

Crystal data for $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$

Formula		$NiOS_2N_7C_{27}H_{51}$
M_r		612.549
Crystallographic system		monoclinic
Space group		$C\,2/c$
Cell dimensions	a	144.09(5) pm
	b	172.51(3) pm
	c	140.81(3) pm
	β	109.32(2)°
	V_c	$3303.0(21) \times 10^{-30}$ m^3
Z		4
D_m		1.22 g cm^{-3}
D_c		1.21 g cm^{-3}
Number of data collected		2485
Number of data with $I \geqslant 1.96\,\sigma(I)$		1613
$F(000)$		1320

Table 2

Fractional coordinates of nonhydrogen atoms with esd in parentheses

Atom	x/a	y/b	z/c
Ni	0.0	0.099	0.25
N	0.0734(4)	0.1050(3)	0.4013(4)
C	0.1246(5)	0.1245(4)	0.4792(5)
S	0.3037(1)	0.3455(1)	0.4094(1)
N (2)	0.5	0.4754(4)	0.25
C(21)	0.4237(6)	0.4346(5)	0.1752(7)
C(22)	0.4232(6)	0.3499(4)	0.1752(6)
C(23)	0.5	0.3054(7)	0.25
N (4)	0.1362(4)	0.1117(3)	0.2120(4)
C(41)	0.2280(6)	0.1275(5)	0.2963(6)
C(42)	0.3127(6)	0.1548(6)	0.2611(6)
C(43)	0.3283(6)	0.0994(6)	0.1769(6)
C(44)	0.2311(6)	0.0853(6)	0.0961(6)
C(45)	0.1495(6)	0.0596(5)	0.1347(6)
N (5)	0.0452(4)	0.3103(3)	0.4313(4)
C(51)	0.0558(6)	0.3958(5)	0.4283(6)
C(52)	0.0405(6)	0.4339(5)	0.1366(7)
C(53)	0.1238(6)	0.4102(5)	0.0955(7)
C(54)	0.1312(6)	0.3204(5)	0.0874(6)
C(55)	0.0297(6)	0.2873(4)	0.0228(6)
O	0.0	0.2254(4)	0.25

Table 3

Anisotropic thermal parameter coefficients $B_{ij}/(10^{-20}\ \mathrm{m}^2)$

Atom	$\{B_{11}\}$	$\{B_{22}\}$	$\{B_{33}\}$	$\{B_{12}\}$	$\{B_{13}\}$	$\{B_{23}\}$
Ni	3.03(7)	2.90(6)	2.66(6)	0.0	0.62(5)	0.0
N	4.13(34)	4.54(35)	2.80(29)	−0.42(31)	0.31(26)	−0.35(29)
C	3.22(37)	3.19(38)	3.44(38)	0.30(30)	1.30(32)	0.38(29)
S	4.51(12)	6.19(14)	3.32(10)	−0.02(11)	0.22(9)	−0.84(10)
N(2)	4.32(51)	2.72(45)	4.14(48)	0.0	0.07(42)	0.0
C(21)	5.38(52)	3.48(43)	7.29(59)	−0.30(41)	−2.00(46)	0.99(41)
C(22)	5.53(52)	3.32(43)	6.06(52)	−0.20(41)	0.32(43)	−0.34(40)
C(23)	5.13(73)	3.84(64)	6.82(81)	0.0	−0.43(65)	0.0
N(4)	2.85(29)	5.28(37)	3.11(28)	−0.41(28)	1.13(24)	−0.25(27)
C(41)	3.55(41)	8.27(65)	4.07(42)	−1.76(41)	1.04(35)	−1.46(40)
C(42)	3.19(42)	10.10(68)	5.54(50)	−2.75(46)	1.87(39)	−2.37(50)
C(43)	3.75(49)	9.36(68)	4.88(45)	0.12(50)	1.72(38)	−0.22(50)
C(44)	4.40(46)	10.67(79)	5.03(48)	−1.94(50)	2.63(42)	−2.17(51)
C(45)	4.61(46)	6.73(53)	4.41(43)	−1.02(41)	2.81(38)	−1.94(39)
N(5)	4.12(35)	3.45(34)	5.26(37)	0.71(28)	1.54(31)	−0.44(29)
C(51)	4.85(46)	3.96(43)	6.85(52)	0.12(42)	2.47(42)	0.14(44)
C(52)	4.83(50)	5.41(51)	6.54(54)	−1.57(41)	2.22(44)	−1.90(42)
C(53)	4.57(48)	4.82(52)	7.83(59)	−1.39(41)	1.53(45)	−0.14(45)
C(54)	4.04(46)	4.77(51)	7.14(58)	−0.18(39)	1.82(43)	0.51(43)
C(55)	5.18(49)	3.77(43)	4.77(45)	−0.50(37)	1.78(40)	−0.26(35)
O	3.34(41)	1.35(34)	2.22(35)	0.0	0.91(32)	0.0

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

The intensity data of independent diffractions in the range $0° < 2\theta \leq 55°$ were collected with Mo$K\alpha$ radiation using a graphite monochromator by $\theta - 2\theta$ technique. They were corrected for Lorentz and polarization factors but no absorption correction was made ($\mu = 7.758\ \text{cm}^{-1}$ and the average dimension of crystal was 0.03 cm).

The crystal structure was determined by heavy atom method and refined by full matrix least-squares method anisotropically to $R = 8.5\ \%$.

The asymmetric unit of the crystal contains 21 nonhydrogen atoms. Their fractional coordinates and anisotropic temperature factors coefficients are listed in Tables 2 and 3. Fractional coordinates of hydrogen atoms calculated from the assumption of sp^3 and sp^2 hybridization, respectively, are given in Table 4.

Table 4

Fractional coordinates of hydrogen atoms*

Atom	x/a	y/b	z/c
H (1) (O)	−0.037	0.268	0.189
H (2) (O)	0.037	0.268	0.310
H (3) (C21)	0.371	0.463	0.123
H (4) (C22)	0.374	0.323	0.123
H (5) (C23)	0.553	0.271	0.250
H (6) (N4)	0.126	0.165	0.175
H (7) (C45)	0.086	0.062	0.076
H (8) (C45)	0.166	0.007	0.164
H (9) (C44)	0.214	0.136	0.067
H(10) (C44)	0.422	0.044	0.050
H(11) (C43)	0.378	0.123	0.150
H(12) (C43)	0.353	0.058	0.211
H(13) (C43)	0.257	0.088	0.335
H(14) (C42)	0.376	0.156	0.320
H(15) (C41)	0.215	0.178	0.340
H(16) (C41)	0.302	0.217	0.231
H(17) (N5)	0.052	0.298	0.502
H(18) (C51)	0.125	0.413	0.476
H(19) (C51)	0.001	0.422	0.444
H(20) (C52)	0.031	0.491	0.125
H(21) (C52)	−0.029	0.406	0.093
H(22) (C53)	0.187	0.430	0.141
H(23) (C53)	0.110	0.433	0.037
H(24) (C54)	0.151	0.297	0.156
H(25) (C54)	0.181	0.307	0.054
H(26) (C55)	0.037	0.234	0.006
H(27) (C55)	−0.026	0.322	−0.037

* Hydrogen atoms positions were calculated after refinement of the structure considering the sp^3 and sp^2 hybridization of C atoms, respectively, with C—H bond length 10.0 pm.

The Fourier syntheses were calculated on Siemens 4004 computer by DRF program (written by A. Zalkin, California, U.S.A. and modified by O. Lindgren, Sweden). The refinement of the structure and additional calculations were performed on the minicomputer Nova 1200 of the computing module XTL of the Syntex diffractometer using the FMLS, DISTAS, and PLANE programs.

Discussion

The crystals of $Ni(NCS)_2(pipe)_2(py)H_2O \cdot 2pipe$ have a molecular structure. The Ni(II) atom is pseudooctahedrally coordinated by two N atoms from the NCS groups (Ni—N being 20.64 pm), two N atoms from the piperidine molecules (with Ni—N^1 22.08 pm), one N atom from the pyridine molecule (Ni—N^2 being 21.48 pm) and one O atom from the coordinated water molecule (Ni—O being 21.65 pm). The interatomic distances and the bond angles are given in Tables 5 and 6. The crystal and molecular structure is shown in Fig. 1.

Table 5

Interatomic distances with esd in parentheses

Atoms	d/pm
Ni —N	20.64 (6)
Ni —N (2)	21.48 (9)
Ni —N (4)	22.08 (6)
Ni —O	21.65 (7)
N —C	11.47(10)
C —S	16.48 (8)
N (2)—C(21)	14.30(11)
C(21)—C(22)	14.62(12)
C(22)—C(23)	14.67(11)
N (4)—C(41)	14.80(11)
C(41)—C(42)	15.65(14)
C(42)—C(43)	15.65(14)
C(43)—C(44)	15.21(13)
C(44)—C(45)	15.16(14)
C(45)—N (4)	14.73(10)
N (5)—C(51)	14.85(11)
C(51)—C(52)	15.36(13)
C(52)—C(53)	15.50(14)
C(53)—C(54)	15.59(13)
C(54)—C(55)	15.53(13)
C(55)—N (5)	14.84(12)
O —N (5)	28.67(10)

Table 6

Bond angles with esd in parentheses

Bonds	Angles/°
N —Ni —N (2)	92.4(2)
N —Ni —N (4)	92.7(2)
N —Ni —O	87.5(2)
N (2)—Ni —N (4)	95.3(2)
N (4)—Ni —O	84.7(1)
C(21)—N (2)—C(21)	121.0(6)
N (2)—C(21)—C(22)	119.6(7)
C(21)—C(22)—C(23)	121.3(7)
Ni —N (4)—C(41)	116.8(4)
Ni —N (4)—C(45)	117.8(4)
C(41)—N (4)—C(45)	113.7(6)
N (4)—C(41)—C(42)	112.9(7)
C(41)—C(42)—C(43)	111.6(7)
C(42)—C(43)—C(44)	110.2(7)
C(43)—C(44)—C(45)	113.2(8)
C(44)—C(45)—N (4)	113.0(7)
Ni —N —C	162.8(6)
N —C —S	178.8(7)
C(51)—N (5)—C(55)	112.0(6)
N (5)—C(51)—C(52)	111.1(7)
C(51)—C(52)—C(53)	108.9(7)
C(52)—C(53)—C(54)	111.6(7)
C(53)—C(54)—C(55)	109.5(7)
C(54)—C(55)—N (5)	109.0(6)

It is evident that the heterocyclic ligands in the complex *I* differ by their steric and also by their electronic properties and one can hardly estimate the degree of contribution of different ligands to the shape and dimensions of the coordination polyhedron. The comparison of the interatomic distances in the coordination sphere of the title complex with those in the complex $Ni(NCS)_2(qn)_4(H_2O)_2$ [5], where qn is quinoline (Ni—N(NCS) being 20.38 pm, Ni—N(qn) being 21.84 pm, Ni—O(H_2O) is 21.28 pm and O—H...N_2(qn) distance is 28.12 pm), shows that all interatomic distances in the complex *I* are longer than their analogues in the quinoline complex. The interatomic distance Ni—N(py) in complex *I* is longer by 1.35 pm in average than the corresponding distances in the complexes of $Ni(NCS)_2(py)_4$ [6] (Ni—N(py) being 20.3 pm) and of $NiCl_2\,(py)_4$ (where Ni—N(py) is 20.0 pm) [7]. It may be concluded that the described differences are caused by different *trans* influence of ligands and due to this fact the interatomic distance Ni—N(py) depends on the character of the ligand in *trans* position.

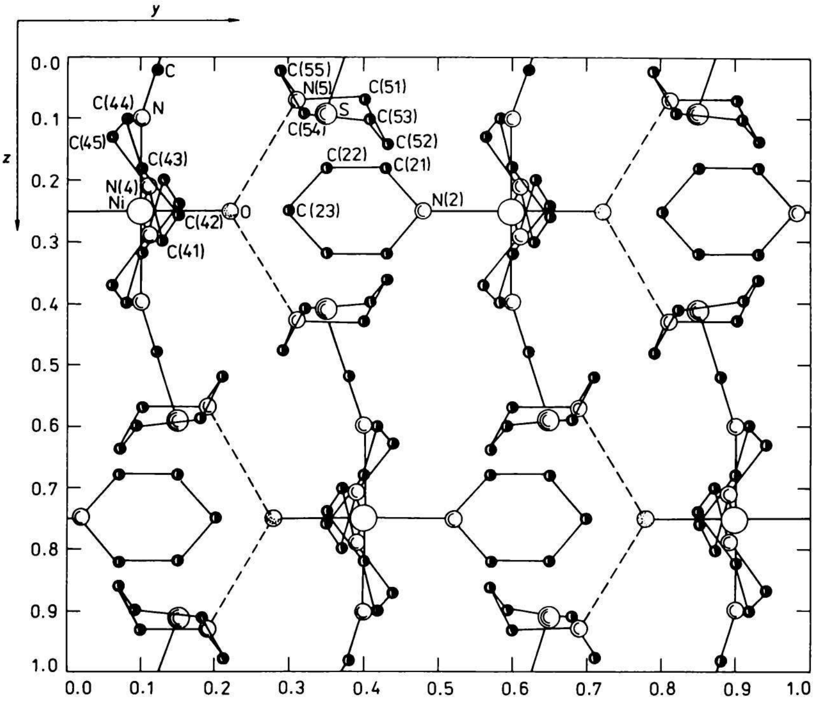

Fig. 1. Packing of the molecules. Projection along the *a* axis.

The NCS group in the complex *I* is bonded terminally to the Ni(II) atom through the N atom similarly as in the complexes Ni(NCS)$_2$L$_4$, where L is py or pipe, respectively [4, 6].

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