

Structural investigations of nickel(II) complexes

III. Crystal structure of Ni(NCS)₂(piperidine)₄

^aM. KOMAN, ^bM. HANDLOVIČ, ^aE. ĎURČANSKÁ, and ^aJ. GAŽO

^aDepartment of Inorganic Chemistry, Slovak Technical University,
CS-812 37 Bratislava

^bInstitute of Inorganic Chemistry, Centre of Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava

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Complex compound Ni(NCS)₂(pipe)₄ crystallizes in orthorhombic system with the space group *C* 222₁ and unit cell dimensions *a* = 76.08 pm, *b* = 194.96 pm, *c* = 176.03 pm, and *Z* = 4. The crystal structure was determined by heavy atom method and refined by least-squares method isotropically to *R* = 10.8 %.

The Ni(II) atom is pseudooctahedrally coordinated by two N atoms from the NCS groups with Ni—N distance 20.0 pm and by four N atoms from piperidine molecules with two different Ni—N distances: Ni—N(1) 22.8 pm and Ni—N(2) 23.6 pm (two pairs of piperidine molecules in *cis* position). The NCS groups are bonded terminally through the nitrogen atoms.

Комплексное соединение Ni(NCS)₂(pipe)₄ имеет следующие структурные характеристики: орторомбическая сингония, пространственная группа *C* 222₁, *a* = 76,08 пм, *b* = 194,96 пм, *c* = 176,03 пм и *Z* = 4. Кристаллическая структура была определена методом тяжелого атома и уточнена изотропно с помощью МНК до *R* = 10,8 %.

Атом Ni(II) обладает псевдооктаэдрической координационной сферой, которую образуют два атома N NCS-группы (длина связи Ni—N = 20,0 пм) и четыре атома N пиперидиновых молекул: Ni—N(1) = 22,8 пм (две молекулы пиперидина в *цис*-положении) и Ni—N(2) = 23,6 пм (две другие молекулы пиперидина в *цис*-положении). Обе NCS-группы являются монодентатными и связаны через атом азота.

From the structural data of nickel(II) complexes with aromatic heterocyclic N-donor ligands it has been concluded that the stereochemical and also other properties of Ni(II) pyridine complexes are influenced by the nature and position of a substituent in the pyridine ligands [1, 2].

The present paper deals with the complex compound Ni(NCS)₂L₄, where L is the piperidine, the saturated analogue of pyridine. The structural data of the title

compound compared with those of pyridine complexes give us information on the influence of electronic and steric properties of various N-donor heterocyclic ligands on the structural and bonding properties of their Ni(II) complexes.

Experimental

Preparation of Ni(NCS)₂(pipe)₄ and indirect structural methods results

The preparation of the complex compound Ni(NCS)₂(pipe)₄ has been described by Eglli and Ludwig [3]. A powder compound formed by their synthesis was not suitable for single crystal X-ray analysis. That is why the preparation of Ni(NCS)₂(pipe)₄ was modified as follows: 3.49 g of Ni(NCS)₂ (0.02 mol) was suspended in 50 cm³ of benzene and 10 cm³ (0.10 mol) of piperidine was added. This system had been boiled at stirring under the reflux condenser for 5 h. Then the suspension was poured into a crystallizing dish and let crystallize freely for 15–20 h. Blue crystals resulted, the chemical analysis of which led to the formula Ni(NCS)₂(pipe)₄ (the observed values: 11.76 % Ni, 16.60 % N, 50.95 % C, and 8.99 % H; the calculated values: 11.39 % Ni, 16.30 % N, 51.26 % C, and 8.60 % H).

In the electronic spectra two absorption maxima at $\tilde{\nu} = 15\,000\text{ cm}^{-1}$ and $\tilde{\nu} = 26\,000\text{ cm}^{-1}$ were observed. They represent the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g}(P) \rightarrow {}^3A_{2g}$ transitions and show that the Ni(II) atom is octahedrally coordinated. The absorption maximum in the region of $\tilde{\nu} = 7000\text{--}11\,000\text{ cm}^{-1}$ caused by the ${}^3T_{2g} \rightarrow {}^3A_{2g}$ transition could not be registered by the apparatus used (Specord UV VIS 200, Zeiss, Jena).

The positions and the character of the i.r. spectra maxima show the terminal bonding of the NCS groups through the N atom: $\tilde{\nu}(\text{CN}) = 2090\text{ cm}^{-1}$, $\tilde{\nu}(\text{CS}) = 810\text{ cm}^{-1}$, and $\tilde{\nu}(\text{N—C—S}) = 487\text{ cm}^{-1}$ (i.r. spectra were measured in nujol by Specord 75 IR).

Thermal decomposition of the title compound starts at 60 °C and in the first step two molecules of piperidine are released from the complex. The second step of thermal decomposition starts at 105 °C and the third one at 205 °C. Each of them corresponds to the release of one piperidine molecule from the complex.

Determination of the structure

The basic crystallographic data were determined using the oscillation and the Weissenberg photographs, and refined using the positions of ten diffractions centred on Syntex P2₁ automatic diffractometer. They are reported in Table 1. Intensity data were collected according to Table 2. The intensities of diffractions were corrected for Lorentz and polarization factors. Since the μ_R value was 0.276, no absorption correction was made.

The crystal structure was determined by heavy atom method and refined by full matrix least-squares method isotropically to $R = 10.8\%$ because of low number of "observed" diffractions (623) with intensity $I \geq 1.96 \sigma(I)$. The small number of nonzero intensities explains also some higher values of temperatures factor coefficients and of the standard deviations of the bond angles. The asymmetric unit of the crystal contains 16 nonhydrogen

Table 1. Crystal data for Ni(NCS)₂(pipe)₄

Formula	NiN ₆ S ₂ C ₂₂ H ₄₄
<i>M_r</i>	515.496
Crystallographic system	orthorhombic
Space group	<i>C</i> 222 ₁
Cell dimensions	<i>a</i> 76.08(5) pm <i>b</i> 194.96(11) pm <i>c</i> 176.03(14) pm <i>V_c</i> 2611.033 × 10 ⁻³⁰ m ³
<i>Z</i>	4
<i>D_m</i>	1.26 g cm ⁻³
<i>D_c</i>	1.31 g cm ⁻³
Number of data collected	1678
Number of data with <i>I</i> ≥ 1.96 σ(<i>I</i>)	623
<i>F</i> (000)	1112

Table 2. Conditions of intensity data collection

Radiation	MoKα (λ) = 7.1069 pm
Monochromator	graphite
Crystal dimensions (average)	0.04 cm
Scan mode	θ:2θ
Scan speed/(°/min)	4.88—29.3
Scan range	± 1° from the peak centre
Check diffractions	2 every 98 diffractions; no decay
Data collection limits	0° < 2θ ≤ 55°

Table 3

Fractional coordinates and isotropic thermal parameters *B*/(10⁻²⁰ m²) of atoms with esd in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	{ <i>B</i> }
Ni	0.0	0.2531 (7)	0.25	3.0 (1)
N	0.2143(24)	0.2529(39)	0.3162 (8)	3.8 (4)
C	0.3290(31)	0.2536(44)	0.3570(11)	3.9 (5)
S	0.4844(11)	0.2427 (7)	0.4212 (3)	4.5 (1)
N (1)	0.1289(33)	0.1695(14)	0.1776(15)	1.1 (1)
C(11)	0.1953(43)	0.1056(16)	0.2193(19)	4.7 (9)
C(12)	0.3263(37)	0.0666(15)	0.1704(17)	2.2 (6)
C(13)	0.2197(54)	0.0364(20)	0.0979(28)	5.2(11)
C(14)	0.1236(44)	0.0969(18)	0.0560(20)	3.0 (8)
C(15)	0.0307(55)	0.1332(15)	0.1160(16)	3.9 (8)
N (2)	0.1524(40)	0.3305(18)	0.1706(20)	4.3 (9)
C(21)	0.2518(39)	0.3786(13)	0.2172(14)	1.5 (5)
C(22)	0.3798(46)	0.4223(18)	0.1627(21)	4.8 (9)
C(23)	0.2633(50)	0.4512(18)	0.0972(25)	4.1 (2)
C(24)	0.1769(48)	0.3941(20)	0.0579(23)	4.1(10)
C(25)	0.0474(35)	0.3473(12)	0.1043(14)	1.6 (6)

atoms. The difference Fourier synthesis showed the maximal residual electron density to be $1.56 \text{ e}^-/10^{-30} \text{ m}^3$. The positional and thermal parameters of the atoms with the estimated standard deviations are listed in Table 3.

All programs used during the determination and refinement of the structure were from the XTL program system supplied by the Syntex corporation.

Structure description and discussion

The crystals of $\text{Ni}(\text{NCS})_2(\text{pipe})_4$ have a monomeric molecular structure (Fig. 1). The Ni(II) atom exhibits a distorted octahedral coordination by two N atoms from the NCS groups, two N(1) and two N(2) atoms from the piperidine ligands. The Ni—N, Ni—N(1), and Ni—N(2) distances are 20.0 pm, 22.8 pm, and 23.6 pm, respectively (Table 4). The bond angles N—Ni—N in the coordination polyhedron are near to 90° (Table 5).

The equatorial plane of the complex is formed by four N atoms from the piperidine molecules (Ni—N(1, 2) (average) being R_c) and the axial positions are occupied by two N atoms from the NCS groups (Ni—N being R_a). The values of the

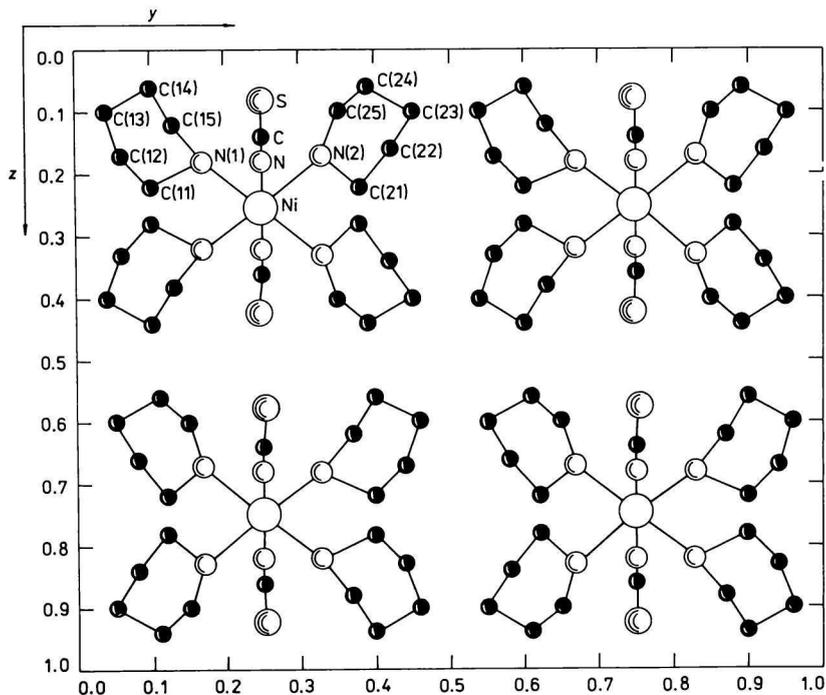


Fig. 1. Packing of the molecules. Projection along the a axis.

Table 4

Interatomic distances with esd in parentheses

Atoms	<i>d</i> /pm
Ni —N	20.0(1)
Ni —N (1)	22.8(2)
Ni —N (2)	23.6(3)
N —C	11.3(2)
C —S	16.5(2)
N (1)—C(11)	15.3(4)
C(11)—C(12)	15.2(4)
C(12)—C(13)	16.2(6)
C(13)—C(14)	15.7(5)
C(14)—C(15)	14.5(5)
C(15)—N (1)	14.9(4)
N (?)—C(21)	14.6(5)
C(21)—C(22)	16.1(5)
C(22)—C(23)	15.6(5)
C(23)—C(24)	14.7(5)
C(24)—C(25)	15.7(4)
C(25)—N (2)	14.5(4)

Table 5

Bond angles with esd in parentheses

Bonds	Angles/°
N (1)—Ni —N (2)	85.1(1)
N —Ni —N (1)	88.5(1)
N —Ni —N (2)	86.9(1)
Ni —N —C	176.0(4)
N —C —S	170.8(5)
Ni —N (1)—C(11)	116.9(1)
Ni —N (1)—C(15)	121.7(2)
N (1)—C(11)—C(12)	110.6(2)
C(11)—C(12)—C(13)	107.4(2)
C(12)—C(13)—C(14)	109.1(3)
C(13)—C(14)—C(15)	104.5(2)
C(14)—C(15)—N (1)	120.8(2)
Ni —N (2)—C(21)	109.4(2)
Ni —N (2)—C(25)	110.4(2)
N (2)—C(21)—C(22)	108.5(2)
C(21)—C(22)—C(23)	106.7(2)
C(22)—C(23)—C(24)	109.1(3)
C(23)—C(24)—C(25)	118.4(3)
C(24)—C(25)—N (2)	101.7(2)

C—C interatomic distances in the piperidine ligands range from 14.5 to 16.2 pm, corresponding to $\geq\text{C—C}\leq$ single bonds [4].

The comparison of the Ni—N distances in the complex $\text{Ni}(\text{NCS})_2(\text{pipe})_4$ (R_e , R_a or R_e/R_a , respectively; R_e/R_a may be considered a measure of the relative tetragonal distortion [5]) with those in complexes $\text{Ni}(\text{NCS})_2\text{L}_4$, where L is NH_3 , pyridine (py) or 4-methylpyridine (4-Mepy), respectively, shows the influence of the ligand properties (electronic and steric) on the structural parameters of coordination polyhedra. The equatorial planes of these complexes are formed by N atoms of neutral ligands and the N atoms of NCS groups are bonded in axial directions as it is in the piperidine complex. The interatomic distances R_e , R_a or R_e/R_a , respectively, in coordination polyhedra of compared compounds are listed in Table 6. They indicate the decrease of R_a distance (the axial one) in the piperidine complex by 0.8 pm in average, in comparison with those of the analogical pyridine and 4-methylpyridine complexes. The R_e/R_a value in the piperidine complex is 1.16. These data allow us to conclude that the change of electronic and steric properties of ligands influences the shape and the interatomic distances "central atom—ligands" in coordination polyhedra of Ni(II). The R_e/R_a difference in the NH_3 and piperidine complexes can be assumed to be caused

Table 6

Structural data for coordination sphere of Ni(II) complexes with NH_3 , aromatic heterocyclic ligands, and piperidine

Compound	Bond	Bond length <i>d</i> /pm	R_e/R_a	Ref.
$\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$	Ni—N(NCS)	20.98(6)	1.020	[6]
	Ni—N(1)(NH_3) I	20.95(8)		
	Ni—N(2)(NH_3) II	21.87(8)		
$\text{Ni}(\text{NCS})_2(\text{py})_4$	Ni—N(NCS)	21.2	0.957	[7]
	Ni—N(py)	20.3		
$\beta\text{-Ni}(\text{NCS})_2(4\text{-Mepy})_4$	Ni—N(NCS)	20.64	1.029	[8]
	Ni—N(4-Mepy) I	21.27		
	Ni—N(4-Mepy) II	21.29		
$\alpha\text{-Ni}(\text{NCS})_2(4\text{-Mepy})_4$	Ni—N(NCS) I	20.66	1.029	[9]
	Ni—N(NCS) II	20.70		
	Ni—N(4-Mepy) I	21.34		
	Ni—N(4-Mepy) II	21.22		
	Ni—N(4-Mepy) III	21.23		
	Ni—N(4-Mepy) IV	21.32		
$\text{Ni}(\text{NCS})_2(\text{pipe})_4$	Ni—N(NCS)	20.0(1)	1.16	
	Ni—N(pipe) I	22.8(2)		
	Ni—N(pipe) II	23.6(3)		

mainly by the steric factors (significantly different volumes of N-donor ligands at analogical σ -donor Ni—N bonding).

On the other hand, the Ni(II) complexes with py or 4-Mepy as ligands exhibit the differences of R_c/R_a values compared to the analogical pipe complex probably because of the differences in the electronic properties of ligands: while the pipe N-donor atom forms only σ -donor bond with the Ni(II) atom, the pyridine N atom is able to form also π -acceptor bond.

The bonding mode of the NCS group in the complex Ni(NCS)₂(pipe)₄ is the same as it is in the complexes Ni(NCS)₂L₄, where L is py, 4-Mepy or ammonia, respectively: it is bonded terminally through the N atom.

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