

# Isomerism of Nickel(II) Complexes. II. Conditions of Formation and Structure of Isomers $\text{Ni}(\text{NCS})_2(\text{Quinoline})_2$

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Two isomers: red (*I*) and green (*II*) of composition  $\text{Ni}(\text{NCS})_2\text{Q}_2$  (Q — quinoline) were prepared by thermal decomposition of solid  $\text{Ni}(\text{NCS})_2\text{Q}_4 \cdot 2\text{H}_2\text{O}$ . The reaction proceeded under isothermal conditions in dependence of the layer thickness and grain size. The structure of isomers was examined by means of the diffuse reflectance and infrared absorption spectra as well as by magnetic measurements. It has been found that isomer *I* shows the  $^1\text{A}_{1g}$  singlet ground state and it can be assigned a monomolecular square-planar configuration with the terminal NCS groups. Isomer *II* shows a six-coordinate tetragonal bipyramidal structure with the  $^3\text{B}_{1g}$  triplet ground state and with two differently coordinated NCS groups (terminal and bridged).

It is the square-planar arrangement of ligands that is characteristic for  $d^8$  electronic configuration and that occurs most often with the elements of the Ni sub-group, mainly Pd and Pt. For Ni(II), however, the paramagnetic octahedral and tetrahedral complexes are very common. With regard to such a variety of coordination polyhedrons there is a topical problem concerning the nickel(II) complexes: what are the causes of the formation and changes of coordination polyhedrons of certain type; with this is closely connected the study of configuration isomerism [1, 2]. Evidently, an important role at the formation of various configuration isomers plays the question to what extent  $\sigma$ - and  $\pi$ -bonds contribute to the overall bonding in complexes. It is therefore interesting to investigate the nickel(II) coordination compounds, especially with ligands having besides  $\sigma$ -donor ability also  $\pi$ -acceptor or  $\pi$ -donor abilities. In this view the suitable ligands appear to be quinoline [3] and the thiocyanate group [4], for which, moreover, both terminal and bridging coordinations are possible.

In our work we concentrate on the study of mechanism of the formation and thermal decomposition of the known isomers [5], red (*I*) and green (*II*) of composition  $\text{Ni}(\text{NCS})_2\text{Q}_2$  (Q — quinoline), regarding their chemical structure and properties. This investigation is a part of the research the aim of which is to gather the information on mechanisms of the substitution reactions of nickel(II) complexes in the solid state [6, 7]. Conditions of the formation of the above isomers by thermal decomposition of the same solid complex  $\text{Ni}(\text{NCS})_2\text{Q}_4 \cdot 2\text{H}_2\text{O}$  and the results of their spectral and magnetochemical investigation in the solid state are described in this paper.

## Experimental

### *Chemicals and analytical methods*

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  anal. grade, KNCS anal. grade, and quinoline anal. grade were of Czechoslovak make (Lachema). Quinoline was purified twice before use by distillation under reduced pressure.

The nickel content was determined complexometrically with murexide used as an indicator. The nitrogen and hydrogen contents were determined by usual method of elemental organic analysis.

### Preparation of compounds

The preparation of thiocyanato-nickel(II) complex with quinoline at molar ratio Ni : Q = 1 : 4 has been described by several authors [5, 8, 9].

The following procedure was used in our work: NiCl<sub>2</sub> · 6H<sub>2</sub>O (0.04 mole) was dissolved in ethanol (80 ml) under stirring. On dissolution, ground solid KNCS (0.08 mole) was added. Separated KCl was filtered off and quinoline (20 ml) was added into a pure solution of Ni(NCS)<sub>2</sub>. After about 2 days green crystals separated. These were washed with ethanol and air-dried.

For Ni(NCS)<sub>2</sub>(C<sub>9</sub>H<sub>7</sub>N)<sub>4</sub> · 2H<sub>2</sub>O (727.50) calculated: 8.07% Ni, 62.70% C, 11.50% N, 4.40% H; found: 8.04% Ni, 63.30% C, 11.40% N, 4.80% H.

Red isomer *I* was prepared by thermal decomposition of the finely ground solid complex Ni(NCS)<sub>2</sub>Q<sub>4</sub> · 2H<sub>2</sub>O (*III*) packed in a thick layer (minimum thickness 5 mm) or by thermal decomposition of the coarse crystalline *III* in the block at temperature 100–120°C.

For Ni(NCS)<sub>2</sub>(C<sub>9</sub>H<sub>7</sub>N)<sub>2</sub> (*I*) (433.17) calculated: 13.60% Ni, 12.95% N; found: 13.53% Ni, 13.06% N.

Green isomer *II* was prepared by thermal decomposition of the finely ground *III* (layer thickness max. 1 mm) at temperature 110–120°C or by multiple action of ethyl ether on the finely ground starting complex *III* and by final drying of the product obtained in a drier at 110–120°C.

For Ni(NCS)<sub>2</sub>(C<sub>9</sub>H<sub>7</sub>N)<sub>2</sub> (*II*) (433.17) calculated: 13.60% Ni, 12.95% N; found: 13.65% Ni, 12.90% N.

### Apparatus and results of measurements

Infrared absorption spectra of the solid samples in nujol were taken on a double beam spectrophotometer UR-10 (Zeiss, Jena) in the region 400–2300 cm<sup>-1</sup>. The results are given in Table 1. Diffuse reflectance spectra were recorded on a Perkin–Elmer 450 spectrophotometer in the 350–900 nm (28,600–11,100 cm<sup>-1</sup>) region. The samples were mixed in an appropriate ratio with MgCO<sub>3</sub>, which was used simultaneously as

Table 1

Infrared spectroscopic data [cm<sup>-1</sup>]

Quinoline free	—		813,	796			746
Isomer <i>I</i>	2107		854,	811,	790,		743
Isomer <i>II</i>	2153,	2114	814,	795,	775,	750,	742

a standard. From the measured reflectance values the values of  $-\log f(R_{\infty})$  were computed [10]. Diffuse reflectance spectra of the isomers investigated are shown in Fig. 1.

A detailed description of the magnetic measurements is presented in the work [11]. The results of magnetic measurements are compiled in Table 2.

## Discussion

*Downs and Ongley* [5] assume the existence of two configuration isomers for the compounds of the type  $\text{Ni}(\text{NCS})_2\text{L}_2$  (L is 2- or disubstituted derivative of pyridine, quinoline or isoquinoline, respectively). In the first place a pair of isomers  $\text{Ni}(\text{NCS})_2\text{Q}_2$  is mentioned. Green isomer was prepared by the action of ether on the dithiocyanato-tetraquinoline nickel(II) complex. By heating this isomer at  $120^\circ\text{C}$  the red isomer was obtained.

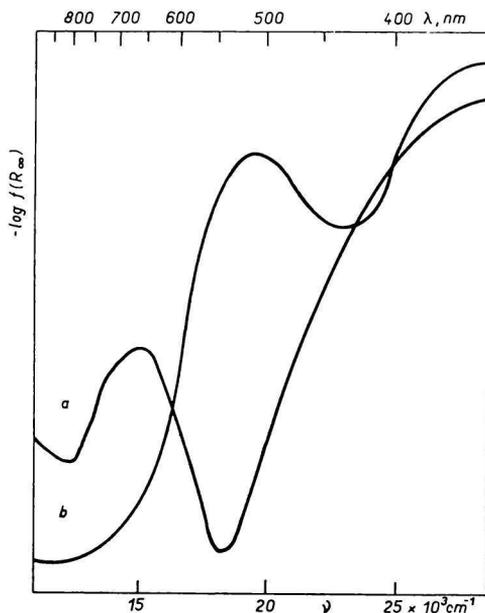


Fig. 1. Diffuse reflectance spectra.  
a) isomer I; b) isomer II.

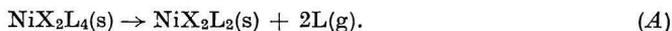
Further details about the formation of the isomers are not known, though it could be of more general validity. From the attempt to prepare them it resulted that:

a) In contrast to [8], from water-alcohol solution there is formed  $\text{Ni}(\text{NCS})_2\text{Q}_4 \cdot \text{Y}$  ( $\text{Y} = 2\text{H}_2\text{O}$ ) and not  $\text{Ni}(\text{NCS})_2\text{Q}_4$ .

b) By the action of ether on  $\text{Ni}(\text{NCS})_2\text{Q}_4 \cdot 2\text{H}_2\text{O}$  there has been obtained green isomer comprising  $\sim 4\%$  of components being released at temperature  $110\text{--}120^\circ\text{C}$ .

c) In contrast to [5], green isomer (II) heated in a drier at  $\sim 120^\circ\text{C}$  is not changed to red isomer (I) but is gradually decomposed into  $\text{Ni}(\text{NCS})_2$ .

It is known from literature [12] that the compounds of the type  $\text{NiX}_2\text{L}_4$  ( $\text{X} = \text{Cl}, \text{Br},$  and  $\text{NCS}$  respectively, and L is a nitrogen-containing organic ligand) are thermally decomposed according to the scheme



Therefore in our further investigation we have concentrated on the question whether it is possible to prepare  $\text{Ni}(\text{NCS})_2\text{Q}_2$  by isothermal decomposition of  $\text{Ni}(\text{NCS})_2\text{Q}_4$ .

Table 2

Magnetic data for isomers Ni(NCS)<sub>2</sub>Q<sub>2</sub> at various temperatures

Complex	Temperature [°K]	$\chi \times 10^6$	$\chi_M \times 10^6$	$\chi'_M \times 10^6$	$\mu_{\text{eff}}$ [B.M.]	$\theta$ [°K]
isomer <i>I</i>	293	-0.24	-104	150	0.59	-
	273	-0.25	-108	146	0.57	
	201	-0.23	-100	154	0.50	
	82	0.00	0	254	0.41	
isomer <i>II</i>	293	9.83	4258	4512	3.17	-17
	273	10.64	4609	4863	3.19	
	201	14.61	6328	6582	3.21	
	82	42.00	18192	18446	3.46	

· 2H<sub>2</sub>O and, if the reaction proceeds according to the scheme (A), which isomer is formed. It has been shown that from the powdered samples most often the mixture of both isomers is formed; this can be expected with respect to the slight differences in their heats of formation [5] (isomer *I*: -15.7 kcal mole<sup>-1</sup>, isomer *II*: -15.3 kcal mole<sup>-1</sup>).

It has been found that in dependence of the layer thickness and grain size it is possible (under equal conditions) to prepare the pure isomer *I* or *II* by isothermal decomposition of the same starting complex. Causes of the formation of particular isomers have to be searched for in the laws of substitution reactions of coordination compounds in the solid state regarding their structure. That is why we examined the spectral and magnetic properties of both isomers in the solid state.

In the diffuse reflectance spectrum of isomer *I* (Fig. 1) a pronounced band is observed at 19,000 cm<sup>-1</sup> in the region determined for the first out of the three bands in the spectrum of the square-planar nickel(II) complexes [13]. Other bands in the near ultraviolet region cannot be identified as they are overlapped by the charge transfer bands and by the bands belonging to the ligands themselves. In the diffuse reflectance spectrum of isomer *II* an absorption band at 15,200 cm<sup>-1</sup> (shoulder at 13 500 cm<sup>-1</sup>) is observed which, however, is overlapped by the band connected with the charge transfer and ligand absorption [14, 15]. On the basis of this and in accord with the data of magnetochemical measurements isomer *II* may be regarded as a paramagnetic pseudooctahedral complex. Since the measurements have not been made at the wave numbers lower than 11,100 cm<sup>-1</sup>, it is impossible to identify the absorption bands unequivocally; but with respect to the predicted NiN<sub>4</sub>S<sub>2</sub> environment a marked tetragonal distortion is considered in this complex. In agreement with the results of other authors [16, 17] the absorption bands at 13,500 cm<sup>-1</sup> (shoulder) and 15,200 cm<sup>-1</sup> can be assigned to the transitions <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>A<sub>2g</sub> and <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>E<sub>g</sub>(F) respectively, and the band at ~24,000 cm<sup>-1</sup> to the <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>E<sub>g</sub>(P) transition in a weak tetragonal field of D<sub>4h</sub> symmetry. Similar splitting of the second band is observed in the diffuse reflectance spectrum of pseudooctahedral complex Ni(NCS)<sub>2</sub>(thiosemicarbazide)<sub>2</sub> [18, 19]; here the tetragonal distortion of the polyhedron has been confirmed also by the X-ray structure analysis [20].

The mode of coordination of the NCS group in these complexes has been investigated by means of the infrared absorption spectra. The thiocyanate group as a ligand

can principally occur as monofunctional, bonded through nitrogen or sulfur, as a bifunctional or trifunctional ligand in the function of a bridge. At coordination of the NCS group the changes of the C—N and C—S stretching vibrations are studied in the first place. It follows from the literary data summarized in [21] that the main criterion of the M—NCS and M—SCN bondings is the band position corresponding to the C—S stretching vibration. The region from 770 to 860  $\text{cm}^{-1}$  is assigned to the M—NCS bonding, from 690 to 730  $\text{cm}^{-1}$  to the M—SCN bonding. For the bridging NCS group the whole mentioned region is determined. Sometimes, however, the interpretation of the spectrum is complicated by the absorption bands of other (mainly organic) ligands. Also in this case the conclusion can be drawn about the coordination in case the absorption band in the second region is missing [22, 23]. It has been shown [24] that the mode of coordination of the NCS group with platinum and palladium complexes of the type  $\text{M}(\text{CNS})_2\text{L}_2$  is dependent to a large extent on the nature of the second ligand. If L is ammonia, NCS group is bonded through sulfur, if L is trialkylphosphine, it is bonded through nitrogen. This can be explained by the metal—sulfur back-donation, which in the case of strong  $\pi$ -acceptor — trialkylphosphine — is so weakened that the M—NCS bonding becomes more stable.

The C—N stretching vibrations of the non-bridging structures are so close that it is difficult to judge the mode of the NCS group bonding in case only this band is used. When investigating the vibrations of analogous compounds in the region 2080—2110  $\text{cm}^{-1}$ , these are ascribed to the M—NCS bonding, in the region 2100 to 2130  $\text{cm}^{-1}$  to the M—SCN bonding [21]. For the bridging thiocyanate group the 2130—2180  $\text{cm}^{-1}$  region is determined [25], that is,  $\sim 30$ —80  $\text{cm}^{-1}$  higher than the corresponding wave numbers of the terminal NCS groups. The regions determined for particular vibrations need not be kept for complexes with different central atoms and various neutral ligands [26], what is often overlooked. For nickel(II) complexes

there have been found only Ni—NCS, Ni—NCS—Ni and Ni—NCS  $\begin{matrix} \text{Ni} \\ \diagdown \\ \text{Ni} \end{matrix}$  coord-

inations from the given possibilities of the NCS group coordination. Compounds of the type  $\text{Ni}(\text{NCS})_2\text{L}_4$ , where L is ammonia, pyridine and its derivatives, show the wave number values in the 2072—2102  $\text{cm}^{-1}$  region for the C—N vibrations and for the C—S vibrations in the region 778—801  $\text{cm}^{-1}$  [24, 26]. The regions 2106—2125  $\text{cm}^{-1}$  and 780—790  $\text{cm}^{-1}$  [27] are assigned to the compounds of the type  $\text{Ni}(\text{NCS})_2\text{L}_2$ , where L is *p*-toluidine, pyridine and its derivatives, for which the polymeric octahedral structure with the bridging bifunctional NCS groups [28] is assumed. When the terminal NCS group in  $\text{Ni}(\text{NCS})_2\text{L}_4$  is changed to the bridging one in  $\text{Ni}(\text{NCS})_2\text{L}_2$ , the shift of the C—S vibration to about 15  $\text{cm}^{-1}$  lower wave numbers and at the C—N vibration to about 30  $\text{cm}^{-1}$  higher wave numbers takes place. In none of the mentioned cases the region determined for the bridging NCS group [21, 25] has been reached. From this point of view  $\text{Ni}(\text{NCS})_2$  is of interest for which the intensive band is observed at 2151  $\text{cm}^{-1}$  (according to [29], and according to [30] at 2165  $\text{cm}^{-1}$ ). This probably is connected with the fact that for  $\text{Ni}(\text{NCS})_2$ , in contrast to the above-mentioned complexes, there is predicted [30] the tetragonal coordination sphere with the bridging but trifunctional NCS groups, probably with the sulfur atoms linked by three bonds.

In the square-planar isomer *I* the band at 2107  $\text{cm}^{-1}$  corresponds to the terminal thiocyanate group. Whether it is bonded through nitrogen or sulfur ensues from the study of the C—S stretching vibration, for which the band at 854  $\text{cm}^{-1}$  has been

identified, this being in accord with  $\nu(\text{C}-\text{S})$  for the square-planar nickel(II) complexes:

$\text{Ni}(\text{NCS})_2(\text{PR}_3)_2$	(860 $\text{cm}^{-1}$ )	[24],
$\text{Ni}(\text{NCS})_2\{\text{P}(n\text{-C}_4\text{H}_9)_3\}_2$	(864 $\text{cm}^{-1}$ ),	
$\text{Ni}(\text{NCS})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	(868 $\text{cm}^{-1}$ )	[31],
$\text{Ni}(\text{NCS})_2(\alpha\text{-picoline})_2$	(856 $\text{cm}^{-1}$ ),	
$\text{Ni}(\text{NCS})_2(2,6\text{-lutidine})_2$	(862 $\text{cm}^{-1}$ )	(measured by authors).

Bonding through nitrogen is supported also by the investigation of the 690 to 730  $\text{cm}^{-1}$  region determined for the  $\text{M}-\text{SCN}$  coordination where, however, any band is missing [21, 22]. Also the band width often suggests what kind of bonding is considered. It has been found for the Pd(II) and Pt(II) complexes [22, 31] that if the thiocyanate group is bonded through sulfur, the spectra with sharp lines above 2110  $\text{cm}^{-1}$  are obtained; in the contrary case, the broad lines below 2110  $\text{cm}^{-1}$  are observed. In the case of isomer *I* the band of medium width below 2110  $\text{cm}^{-1}$  is considered, what also support the view that we take into consideration the Ni—NCS bonding.

For the pseudooctahedral isomer *II* there have been observed two bands: at 2114  $\text{cm}^{-1}$  and 2153  $\text{cm}^{-1}$ ; this is in accord with [5] but it differs from the results of *Clark* and *Williams* [27] who have found for green  $\text{Ni}(\text{NCS})_2\text{Q}_2$  one absorption band at 2110  $\text{cm}^{-1}$ . They do not present either its other properties or data for the red  $\text{Ni}(\text{NCS})_2\text{Q}_2$ . These authors investigated the spectra of several complexes of the type  $\text{M}(\text{NCS})_2\text{L}_2$  and in the five cases they observed two bands for the C—N vibration. This concerns the compounds  $\text{Zn}(\text{NCS})_2\text{L}_2$ , where L is pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_2$  and  $\text{Cu}(\text{NCS})_2(\text{quinoline})_2$  and the mentioned bands are in the regions 2070—2080  $\text{cm}^{-1}$  and 2098—2128  $\text{cm}^{-1}$ , respectively. According to these authors the molecular symmetry requires for all tetrahedral and polymeric octahedral complexes doubling of the band since the group  $\text{SCN}-\text{M}-\text{NCS}$  is not linear. If there is observed only one band they assume a random degeneration. The infrared spectrum of isomer *II* shows two sharp bands practically of the same intensity; the band at 2153  $\text{cm}^{-1}$  is markedly shifted to higher wave numbers than it has been found for the analogous complexes. On the basis of this shift as well as the existence of two C—S vibrations, we suppose the presence of the thiocyanate groups of different coordinate bonds in isomer *II*, that is, terminal (bonded through nitrogen) and bridging, probably trifunctional, as in  $\text{Ni}(\text{NCS})_2$ . This assumption is supported also by the works of *Charitonov et al.* [32, 33]. These authors identified in the thiocyanate complexes of Zn(II) and Cd(II) both terminal and bridged NCS groups (in the same complex) on the basis of two intensive bands at  $\sim 2090$   $\text{cm}^{-1}$  and  $\sim 2150$   $\text{cm}^{-1}$ , for which they found also the corresponding C—S bands. These bands are mostly further split.

Further information on the structure of both isomers was obtained by the investigation of their magnetic properties. In agreement with the obtained spectral data it can be stated that isomer *I* shows the  $^1\text{A}_{1g}$  singlet ground state. It can be deduced from this that this isomer is a monomolecular square-planar complex.

The susceptibility of isomer *II* obeys the Curie—Weiss law, according to which the Weiss constant  $\Theta$ , as determined from the plot of dependence  $1/(\chi'_M - N\alpha)$  on absolute temperature (Fig. 2), attains a considerable negative value ( $-17^\circ\text{K}$ ). It follows from it that the magnetic moment at 293°K increases with decreasing temperature. On this basis [34] isomer *II* may be assigned a six-coordinate octahedral,

more probably tetragonal bipyramidal structure with the  ${}^3B_{1g}$  triplet ground state of  $D_{4h}$  symmetry. Such a structure requires the existence of polymeric system with NCS groups in the function of bridges between Ni(II). The found negative value  $\Theta$  and the temperature dependence  $\mu_{ef}$  show that here the weak ferromagnetic interaction takes place, which is the result of the positive magnetic coupling between the

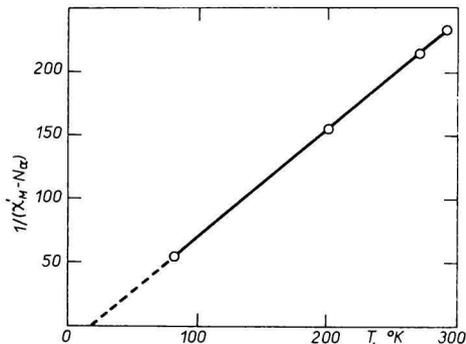


Fig. 2. Graphical representation of the validity of the Curie-Weiss law at isomer II.

cations Ni(II). In case only a part of NCS groups occur as bridges in the polymeric six-coordinate structure, they have to act as trifunctional. It is possible that their sulfur atoms are symmetrically coordinated to Ni(II) and thus, their orbitals may realize [35] a suitable path for the superexchange interaction leading to the observed ferromagnetism. This is in agreement with the works [30, 36], where the ferromagnetic interaction found for complexes  $Ni(NCS)_2$  and  $Ni(NCS)_2(thiourea)_2$ , respectively, has been interpreted similarly.

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