

Isomerism of nickel(II) complexes. VIII.* Study of isomerism of isothiocyanatonickel(II) complexes with some alkylamines

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Complexes of the type $\text{Ni}(\text{NCS})_2\text{B}_n$ (B is methylamine and ethylamine; $n = 2$ and 4) and two isomers of complex $\text{Ni}(\text{NCS})_2(\text{diethylamine})_2$ were prepared. From the spectral and magnetic data it follows that the red isomer has a square-planar configuration with end-bonded NCS groups, while the green isomer is pseudo-octahedral polymer complex with both terminal and bridge-bonded (trifunctional) NCS groups. Complexes $\text{Ni}(\text{NCS})_2\text{B}_n$ have a pseudo-octahedral configuration with end-bonded ($n = 4$) or bridge-bonded ($n = 2$) NCS groups. It was found that the formation of the above-mentioned isomers is connected (besides the appropriate bonding properties of ligands) also with the steric effect of diethylamine in a similar way as in complexes with 2-substituted derivatives of pyridine.

Были приготовлены комплексы типа $\text{Ni}(\text{NCS})_2\text{B}_n$ (B = метиламин и этиламин; $n = 2$ и 4) и два изомеры комплекса $\text{Ni}(\text{NCS})_2(\text{диэтиламин})_2$. Из спектральных и магнитных данных вытекает, что изомер красного цвета имеет квадратную конфигурацию с концевыми NCS группами, в то время как изомер зеленого цвета — псевдооктаэдрический полимерный комплекс обладающий как концевыми NCS группами, так и NCS группами связанными мостиковой связью (трехфункционально). Комплексы $\text{Ni}(\text{NCS})_2\text{B}_n$ имеют псевдооктаэдрическую конфигурацию с концевыми NCS группами ($n = 4$) или связанными мостиковой связью ($n = 2$). Было показано, что образование приведенных изомеров связано (кроме подходящих свойств NCS группы к образованию связи) прежде всего со стерическим эффектом диэтиламина, который аналогичен как в случае 2-замещенных производных пиридина.

The formation of nickel(II) complexes with octahedral square-planar and tetrahedral configurations as well as the formation of configurational isomers [1—3] can be generally affected predominantly by the electronic and steric properties of ligands [4]. From the published data it follows that in the formation of configurational isomers the more important role is attributed to electronic properties, namely to the π -bonding ability of neutral ligands [2, 3, 5].

* For Part VII see Ref. [7].

In order to appreciate the importance of the above two factors on the formation of configurational isomers of the type $\text{Ni}(\text{NCS})_2\text{B}_2$ (B is monofunctional nitrogen ligand) we have aimed our attention at isothiocyanatonickel(II) complexes with aliphatic amines. By introducing primary and secondary amines into the complexes of the given type the contribution of π bonds of neutral ligands is eliminated and hence the influence of steric effect on the composition and properties of the prepared complexes as well as the possibilities of the formation of configurational isomers in solid state can be studied.

Experimental

Chemicals and analytical methods

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ anal. grade, KNCS anal. grade, pyridine anal. grade, and ethylamine "pure" (Lachema, Brno), diethylamine "pure" and methylamine "pure" (Farbica, Allemann) were used.

The nickel content was determined complexometrically with solution of complexon III (0.02) anal. grade (Lachema, Brno) using murexide as indicator. The determination of amines content is analogous to that of ammonium [6].

Preparation of complexes

Preparation of all complexes started from $\text{Ni}(\text{NCS})_2$ obtained by the thermal decomposition of $\text{Ni}(\text{NCS})_2(\text{pyridine})_4$ complex. Preparation of the last complex is analogous to that of

Table I

Composition of the complexes I to V

Complex	M	Calculated/found	
		% Ni	% Amine
I	299.05	19.62	41.53
		19.69	41.45
II	355.14	16.52	50.76
		16.59	50.68
III	236.99	24.77	26.21
		24.83	26.05
IV	265.04	22.15	34.04
		22.18	34.01
V	321.01	18.28	45.53
		18.17	46.02
VI	321.01	18.28	45.53
		18.60	45.12

$\text{Ni}(\text{NCS})_2(\text{quinoline})_4 \cdot 2\text{H}_2\text{O}$ [2]. Complexes $\text{Ni}(\text{NCS})_2(\text{methylamine})_4$ (*I*) and $\text{Ni}(\text{NCS})_2(\text{ethylamine})_4$ (*II*) were prepared by exposing $\text{Ni}(\text{NCS})_2$ for 2 days to the vapours of appropriate amine. Excess amines were removed from resulting light blue compounds by few hours drying above H_2SO_4 . The weight increase was controlled by weighing.

Complexes $\text{Ni}(\text{NCS})_2(\text{methylamine})_2$ (*III*) and $\text{Ni}(\text{NCS})_2(\text{ethylamine})_2$ (*IV*) were prepared by heating the complexes *I* and *II* at temperatures 130 and 110°C, respectively. Decrease of weight was controlled by weighing.

Red isomer of $\text{Ni}(\text{NCS})_2(\text{diethylamine})_2$ (*V*) was prepared by reaction of solid $\text{Ni}(\text{NCS})_2$ with liquid diethylamine. In contact with air it changes into the green isomer (*VI*) [7]. The results of analysis are presented in Table 1. Solid $\text{Ni}(\text{NCS})_2$ does not react with trimethyl- and triethylamine because of steric reasons; with dimethylamine we did not succeed in the preparation of a well defined product.

Instruments

The electronic absorption spectra of the solid samples were measured with a Perkin—Elmer spectrophotometer 450 in the region 6000—28 000 cm^{-1} using a Nujol suspension placed on a chromatographic paper. The infrared absorption spectra of the solid samples (in KBr tablets) were measured with a double-beam UR-10 (Zeiss, Jena) spectrophotometer in the regions 700—900 and 2200 cm^{-1} . Magnetic susceptibilities were measured using Gouy-type magnetic scales (Newport Instruments Ltd.). The effective magnetic moments were calculated according to relations presented in our previous paper [8]. Temperature independent paramagnetism $N\alpha$ was calculated according to formula $N\alpha = 2.09/\Delta$ (where Δ is the ligand-field force) [9].

Results and discussion

Various space arrangements of ligands around the central atom are typical for nickel(II) complexes. If these complexes are of the same composition, it is the case of the so-called configurational isomers [1—3]. A valuable information on the shape of coordination polyhedron can be obtained from the spectral data and the magnetic moments. For the studied complexes these data are presented in Table 2.

The electronic absorption spectra of the complexes *I* and *II* show three simple bands in the measured region (Table 2) with maxima at the wavenumber intervals corresponding to octahedral complexes. This is confirmed by their magnetic moments and also by the analogy between the spectra of complexes *I* and *II*, and of the complex $\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$. The last complex is known to be *trans*-octahedral, which was confirmed also by X-ray analysis [10]. With respect to heterogeneous coordination sphere and in agreement with [11] one could consider a D_{4h} symmetry. However, this symmetry would cause a splitting of individual bands in electronic spectrum. From the X-ray analysis of $\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$ it follows that the deviation from O_h symmetry is rather small, and this is the reason, why the splitting of absorption bands was not observed (measured in Nujol).

Complexes *III*, *IV*, and *VI* differ from the previously discussed ones by the appearance of one or two additional bands between $\tilde{\nu}_1$ and $\tilde{\nu}_2$ (Table 2). The spin-forbidden transition to 1E_g (1D) level could in principle occur in this region. As far as complexes *III* and *IV* are concerned, one has to consider a splitting of 1E_g level since these complexes show two bands in the discussed region. However, such large splitting is unlikely without a simultaneous splitting of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ bands. The additional bands correspond more likely to low-symmetry components of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ bands resulting from D_{4h} symmetry.

Table 2

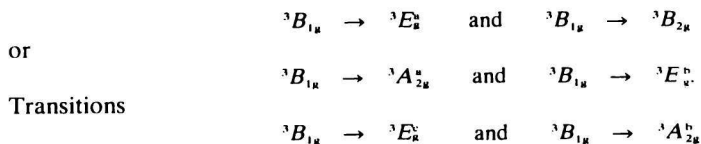
Magnetic moments and spectral data of the complexes in solid state at room temperature

Compound	μ_{eff} B.M.	Electronic absorption spectra. cm^{-1}					Infrared absorption spectra. cm^{-1}		
		$\tilde{\nu}_1$			$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}(\text{C—S})$	$\tilde{\nu}(\text{C—N})$	
I	3.09	10 800			17 200	~28 000 sh	782	2135 w 2108 s	
II	3.07	10 700			17 000	~28 200 sh	789	2130 w 2105 s	2115 w
A	3.23*	10 400			17 150	28 000	785	2108	
III	3.12	8 150	11 700	13 600	16 700	30 150	780	2135	
IV	3.11	8 250	11 700	13 800	16 550	30 000	798 784	2128	
B	3.04	8 200	11 850	13 150	16 750	29 300	788	2125	
V	1.23	19 600			30 450		856	2113	
VI	3.30	9 350	13 130		15 000	25 400	787 775	2082 s 2092 w	2090 w 2130 s

A — $\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$; B — $\text{Ni}(\text{NCS})_2(\text{NH}_3)_2$.

* Presented in Ref. [25].

Values of magnetic moments and infrared spectra of the complexes *III*, *IV*, and *VI* (Table 2) are in agreement with pseudooctahedral configuration with bridging NCS groups. In this case coordination of sulfur atoms of the NCS groups deforms the ligand field to such an extent that there occurs a splitting of the first and second bands in spectra. Taking into account the above-given arguments and literature data [11—14], we incline rather to the second alternative. On this basis it is possible to assign the components of the first two bands for the complexes *III* and *IV* to following transitions



are apparently included in $\bar{\nu}_3$ band, which is already partially overlapped by the charge-transfer band.

The splitting of the first band of complex *VI* was not observed. However, the shape of this band suggests that it contains two close components and the smoothing is caused by the components of vibrational transitions [12]. Magnetic moment of complex *VI* is at the upper limit of values observed for octahedral complexes of nickel(II), but it was shown by *Lever* [15] that tetragonal nickel(II) complexes can have magnetic moments up to 3.5 B.M.

Electronic spectrum of complex *V* differs markedly from the spectra of other compounds studied by the absence of bands below 15 000 cm^{-1} . The intense band with a maximum at 19 600 cm^{-1} is in the region where the first of three bands of square-planar complexes of Ni(II) occurs [16, 22]. The band with a maximum at 30 450 cm^{-1} is probably already overlapped by the charge-transfer band. Analogous data were found for complexes with quinoline [2] and 4-methylquinoline and they were interpreted in the same way. Magnetic moment of complex *V* (1.23 B.M.) is higher than one would logically expect from the temperature independent paramagnetism (≈ 0.8 B.M.). This can be explained by the presence of little amount of paramagnetic isomer *VI* (which is formed due to the relatively fast conversion $V \rightarrow VI$). This explanation is supported by infrared spectra (particularly the $\bar{\nu}(\text{C—S})$ band) and macroscopic observation (different colour on the walls of tube) of complex *V* after the magnetic measurements.

The infrared spectra (in particular stretching vibrations $\bar{\nu}(\text{C—N})$ and $\bar{\nu}(\text{C—S})$) were used to investigate the type of bonding of NCS groups in the studied complexes. Besides the intensive band at 2100 cm^{-1} , one or two weaker bands are observed at higher wavenumbers in spectra of complexes *I* and *II*. This seems to be in contradiction with the assumed *trans*-octahedral structure with end-bonded NCS groups. This case has been observed in the spectra of complexes of the type $\text{Ni}(\text{NCS})_2\text{B}_4$ more frequently [17—19] and can be caused [20] by a deviation of NCS group from linearity, by the Jahn—Teller effect or by other effects which suppress the degeneration of this band. In solid state the lattice interactions can be the predominant factor. The estimation of the type of coordination is therefore based on the position of the main (most intensive) band. Then the intensive bands at 2108 and 2105 cm^{-1} in the spectra of complexes *I* and *II*, respectively, can be assigned to end-bonded NCS group. The $\bar{\nu}(\text{C—S})$ bands at 782 and 789 cm^{-1} , respectively, are in agreement with Ni—N(NCS) bond [2]. In the spectra of complexes *III* and *IV*, bands at 2135 and 2128 cm^{-1} , respectively, occur in the region corresponding to end Ni—S(SCN) [2] or bridge Ni—NCS—Ni group bonded bifunctionally [21]. The absence of a band in 690—730 cm^{-1} region eliminates the first alternative. Analogous $\bar{\nu}(\text{C—N})$ vibrations were observed also in

the spectra of other complexes [12] with assumed polymer structure with bifunctional NCS groups. The intensive band at 2113 cm^{-1} in spectrum of the red isomer (V) can be assigned in agreement with the above-mentioned arguments to end-bonded (probably through the nitrogen atom) NCS group. The $\nu(\text{C—S})$ band is in the region of the square-planar nickel(II) complexes [2, 3] which agrees with the electronic spectra and interpretation of an anomalous magnetic moment. In spectrum of complex VI the strong band at 2082 cm^{-1} unambiguously shows the presence of end-bonded NCS group. Since complex VI exhibits a pseudooctahedral structure (coordination number 6) another NCS group must be bridge-bonded (trifunctionally) and the band at 2130 cm^{-1} corresponds to this bond. Similar results were presented in [19].

From the spectral and magnetic data it follows that complexes I to IV exhibit a pseudooctahedral arrangement with end- (complexes I and II) or bridge-bonded (III, IV, VI) NCS groups. Complex V has a square-planar structure with end-bonded NCS groups. Stereochemistry of the prepared complexes $\text{Ni}(\text{NCS})_2\text{B}_2$ is summarized in Table 3, where for comparison also some analogous complexes with pyridine and its derivatives are presented. This Table shows that of all studied complexes with amines only the complex with diethylamine forms complexes with both pseudooctahedral and square-planar arrangements. Transition from primary to secondary amines is accompanied not only by a reduction of numbers of molecules B bonded to the central atom but also by a change of stereochemistry. Analogous changes were observed with pyridine derivatives (Table 3). The complexes with pyridine derivatives containing a substituent in position 2 (α -substituted derivatives), unlike the ligands with substituent in position 3 or 4, have a square-planar structure or form configurational isomers. These structural differences cannot be explained solely on the basis of electronic properties of neutral ligands. 2- and 4-methyl derivatives of pyridine have nearly the same electronic properties. In spite of it they form complexes with different coordination polyhedrons. In 2-substituted derivative of pyridine the group in position 2 interacts with the nitrogen atom from NCS group and this interaction lowers the structural stability. The structure can be stabilized either by stretching of $\text{Ni—N}(\text{py})$ bonds or by turning the pyridine ring out of equatorial plane, which we believe to be more likely (it is supported also by X-ray data [23]). A turned 2-substituent, however, weakens the interaction in axial direction and supports the formation of a square-planar coordination around the Ni atom. *Goldstein et al.* [24] drew the same conclusions with respect to copper(II) complexes with 2-alkyl derivatives of pyridine. They assume considerable steric hindrances also in complexes with dialkylamines as neutral ligands.

Table 3

Stereochemistry of complexes $\text{Ni}(\text{NCS})_2\text{B}_2$
(\uparrow pseudooctahedral; \square square-planar)

B	py	4-mepy	3-mepy	2-mepy	Q	4-meQ
Stereochemistry	\uparrow	\uparrow	\uparrow	\square	$\square\uparrow$	$\square\uparrow$
B	NH_3	ma	ea	dea	—	—
Stereochemistry	\uparrow	\uparrow	\uparrow	$\square\uparrow$	—	—

py — pyridine, 2(3,4)-mepy: 2(3,4)-methylpyridine; Q — quinoline, 4-meQ: 4-methylquinoline; ma — methylamine; ea — ethylamine; dea — diethylamine.

Thus with an increasing steric effect of neutral ligand the stability of octahedral structure decreases, while the stability of square-planar structure increases. At certain conditions the difference between the total energies of octahedral and square-planar arrangements in solid state is minimum and it is possible to prepare both forms, *i.e.* the configurational isomers. In other cases only square-planar or octahedral form is stable in solid state. In agreement with our conclusions, the experimentally determined energy differences between isomers are relatively small [26]. Hence it follows that even small contributions to the total energy of a system in solid state can play a decisive role for relative stabilities of configurational isomers.

Thus it can be concluded, that for complexes of the type $\text{Ni}(\text{NCS})_2\text{B}_2$ (B is aliphatic amine) formation of octahedral or square-planar configuration (which generally depends on the suitable electronic configuration of Ni(II) and bonding properties of ligands) can be realized even under the influence of such steric requirements of neutral ligands as exhibited by diethylamine.

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