

ISOMERISM OF NICKEL(II) COMPLEXES. V.*

A STUDY OF THE ISOMERISM OF ISOTHIOCYANATE NICKEL(II) COMPLEXES WITH LEPIDINE

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A pair of configurational isomers of $\text{Ni}(\text{NCS})_2\text{B}_2$ (B = lepidine) and several other complexes with lepidine, *i.e.* $\text{Ni}(\text{NCS})_2\text{B}_n \cdot 2\text{H}_2\text{O}$ ($n = 2$ or 4) and $\text{Ni}(\text{NCS})_2\text{B}_4 \cdot \text{H}_2\text{O}$ were prepared. It follows from the electronic and infrared adsorption spectra that the red isomer has a square planar mononuclear configuration with end-bonded Ni-NCS groups, while the green isomer is a pseudo-octahedral polymeric complex with bridge-bonded NCS groups. Both complexes, $\text{Ni}(\text{NCS})_2\text{B}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{NCS})_2\text{B}_2 \cdot 2\text{H}_2\text{O}$ have a mononuclear pseudo-octahedral configuration of the co-ordination sphere $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2\text{B}_2]$. With the complex, $\text{Ni}(\text{NCS})_2\text{B}_4 \cdot \text{H}_2\text{O}$, the co-ordination sphere $[\text{Ni}(\text{NCS})_2\text{B}_3]$ is expected to have a trigonal bipyramidal configuration. Both isomers were prepared by heterogeneous reactions. It seems probable that an important role in their formation is possibly played by the magnitude of the π -bond contribution to the overall bond system in the complexes.

It is known^{1,2} that, among several types of isomerism, configurational isomers, differing in the geometrical configuration of the primary co-ordination sphere, are the most typical for nickel(II) complexes. On the basis of the work by Downs and Ongley³, who assume the existence of several configurational isomers of the type $\text{Ni}(\text{NCS})_2\text{L}_2$ (L = a pyridine derivative), a pair of isomers $\text{Ni}(\text{NCS})_2\text{Q}_2$ (Q = quinoline) was prepared and the conditions for their formation and some structural parameters were characterized^{1,2,4}.

The present paper is aimed at determining whether it is possible to prepare a pair of configurational isomers of the above type also of the quinoline derivative lepidine (4-methylquinoline). For this reason, the conditions for the formation and the spectral properties (electronic and infrared absorption spectra) of several isothiocyanato nickel (II) complexes with lepidine in the solid phase were studied. The aim is to contribute to the knowledge of factors (especially conditions for the preparation and the choice of suitable ligands) which affect the formation of configurational isomers of the above type. With regard to the kinetic lability of Ni(II) complexes in solution, from which the complexes in the solid phase are usually obtained only in one, thermodynamically more stable configuration, we directed our work to hetero-

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geneous systems in which the preparation of some thermodynamically less stable isomers has already been achieved⁵.

EXPERIMENTAL

Reagents and methods. $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, KCNS, and lepidine were of p.a. purity (Lachema, Brno). Lepidine was purified before use by double distillation at lowered pressure. The nickel content was determined complexometrically, using murexide as an indicator. The nitrogen, carbon, and hydrogen contents were determined by common methods of organic elemental analysis.

Preparation of the Compounds

Complexes with a Ni : B molar ratio of 1 : 4 : To 0.04 mol of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ in 100 ml of ethanol were added 0.08 mol finely divided KCNS powder. The precipitated KCl was filtered off and 0.16 mol of lepidine was added to the pure solution. At laboratory temperature, small light green cubic crystals (*I*) were formed within 2 to 3 days; they were washed with ethanol and dried in the air. For $\text{Ni}(\text{NCS})_2(\text{C}_{10}\text{H}_9\text{N})_4 \cdot 2 \text{H}_2\text{O}$ (783.6) calculated: 7.49% Ni, 64.32% C, 10.72% N, 5.15% H; found: 7.51% Ni, 65.04% C, 10.52% N, 5.14% H. Using equal amounts of the starting compounds, but only 50 ml of ethanol, grass green, small, rod-like crystals (*II*) were formed at laboratory temperature. These crystals can be prepared pure by crystallization from the above solutions at a temperature of about 50°C. For $\text{Ni}(\text{NCS})_2(\text{C}_{10}\text{H}_9\text{N})_4 \cdot \text{H}_2\text{O}$ (765.6) calculated: 7.67% Ni, 65.83% C, 10.98% N, 5.00% H; found: 7.64% Ni, 66.21% C, 11.07% N, 5.13% H. Complex *II* is also formed by heating the dihydrate in a sealed ampule at a temperature of 45°C. In a closed space, saturated with water vapour, it is converted to complex *I*, at laboratory temperature. It follows, from the increase of weight, that complex *II* is the monohydrate.

*The red isomer, $\text{Ni}(\text{NCS})_2\text{B}_2$ (*III*)* was prepared by isothermal decomposition of the finely powdered solid complex, *I* or *II*, at a temperature of 90 to 110°C, or by heating complexes *IV* or *V* (see later). For $\text{Ni}(\text{NCS})_2(\text{C}_{10}\text{H}_9\text{N})_2$ (461.2) were calculated: 12.73% Ni, 57.24% C, 12.15% N, 3.93% H; found: 12.68% Ni, 57.18% C, 12.20% N, 4.08% H. In a closed space saturated with water vapour, complex *III* (and also complex *V*) is converted into a light green substance (*IV*). It follows from the weight increase, that the dihydrate is formed, which can also be prepared by treating complex *I* or *II* with diethyl ether. For $\text{Ni}(\text{NCS})_2(\text{C}_{10}\text{H}_9\text{N})_2 \cdot 2 \text{H}_2\text{O}$ (497.2) calculated: 11.81% Ni, 53.09% C, 11.27% N, 4.46% H; found: 11.89% Ni, 52.94% C, 11.41% N, 4.59% H.

*The green isomer, $\text{Ni}(\text{NCS})_2\text{B}_2$ (*V*)* was prepared by the repeated treating of either of complexes *I* or *II* with ether (100 ml of ether reacted with 2.5 g complex *I* or *II* for 30 minutes, with vigorous stirring. The process was repeated twice more with new portions of ether). The preparation was carefully dried at a temperature of 55°C. For $\text{Ni}(\text{NCS})_2(\text{C}_{10}\text{H}_9\text{N})_2$ (461.2) found: 12.61% Ni, 57.09% C, 11.97% N, 4.05% H.

Apparatus and Measuring Results

The electronic absorption spectra of the solid samples were measured with the Perkin-Elmer spectral photometer 450, in the region from 6000 to 28000 cm^{-1} (1670 to 357 nm), using a Nujol suspension placed on a chromatographic paper. The infrared absorption spectra of solid samples were measured with the double-beam spectral photometer UR-10 (Zeiss, Jena) in the regions from 750 to 900 and from 2050 to 2200 cm^{-1} , using a Nujol mull. The results are given in Table I.

TABLE I
Spectral Data for Isothiocyanate Nickel(II) Complexes (in cm^{-1})

Compound	Absorption bands, IR							Absorption bands, UV		
	Lepidin			$\tilde{\nu}_{\text{C-S}}$	$\tilde{\nu}_{\text{H}_2\text{O}}$	$\tilde{\nu}_{\text{C-N}}$				
<i>I</i>	761	773	841	877	788	805	2 122	8 300	13 400 (sh)	25 500 (sh)
		819	847	887				9 400	15 100	
<i>II</i>	764	775	844	875	785	—	2 083	~ 6 000	10 700	14 500 20 700 (sh)
		819	849 (sh)	889			2 097			24 600
<i>III</i>	762	782	838	—	863	—	2 100	19 250		
		814	844							
<i>IV</i>	762	820	846	888	792	841	2 125	8 300	13 500	25 500 (sh)
								9 700	15 300	
<i>V</i>	762	820	846	889	791	—	2 121	8 300 (sh)	13 200 (sh)	25 500 (sh)
					806		2 136	9 400	14 600	
Free B	762	821	848	867	—	—	—	—	—	—

DISCUSSION

The present paper is based on the work of Downs and Ongley³, and also on our own papers^{1,2,4}, dealing with the study of two configurational isomers, $\text{Ni}(\text{NCS})_2$ (quinoline)₂. In an attempt to prepare analogous isomers with lepidine, we found that, in aqueous ethanolic solution, in dependence on the concentration and temperature, is formed not only the complex $\text{Ni}(\text{NCS})_2\text{B}_4 \cdot 2 \text{H}_2\text{O}$ (*I*) (as in the case of the analogous quinoline complexes), but also the complex $\text{Ni}(\text{NCS})_2\text{B}_4 \cdot \text{H}_2\text{O}$ (*II*) while, in a medium containing water vapour, substance *II* is converted into substance *I*. By isothermal decomposition of both substances *I* and *II*, only the red isomer, $\text{Ni}(\text{NCS})_2\text{B}_2$ (*III*), is formed. By the action of ether on solid substances *I* and *II*, the complex $\text{Ni}(\text{NCS})_2\text{B}_2 \cdot 2 \text{H}_2\text{O}$ (*IV*) is formed first, and is converted into the green isomer $\text{Ni}(\text{NCS})_2\text{B}_2$ (*V*), by further action of ether and careful drying. Isomers *III* and *V* are easily hydrated and converted into substance *IV*. The conversions of these complexes are summarized in Fig. 1.

In studying the factors affecting the formation of both isomers, it is advantageous to obtain information about their geometrical configuration and the composition of the primary coordination sphere. For this reason, the spectral properties of the complexes prepared were studied in the solid state.



The electronic spectra of the solid complexes *I* to *V* (Table I) indicate that there are basically three groups considerably differing in their geometrical configuration. The first group includes complexes *I*, *IV*, and *V*, complex *III* belongs in the second group, and complex *II* in the third. The electronic absorption spectra of the first group show two complex absorption bands, in the region from 8300 to 9700 cm^{-1} and 13200 cm^{-1} to 15200 cm^{-1} . A broad band is observed in the region 22000 to 26000 cm^{-1} , and is considerably overlapped by a band connected with the charge-transfer and ligand absorption. On the basis of these data, and in agreement with the results of magneto-chemical measurements⁶ at 293 K (complex *I*: 3.21 B.M., *IV*: 3.17 B.M., *V*: 3.17 B.M.), the complexes from the first group can be considered to be paramagnetic pseudo-octahedral complexes. The essentially identical spectra of the hexaco-ordinated complexes *I* and *IV* reflect identical primary co-ordination spheres $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2\text{B}_2]$. The two lepidine molecules left in complex *I* are probably bounded by a bond of the clathrate type, similar to the complex⁷ $\text{Ni}(\text{NCS})_2 \cdot (\text{quinoline})_4 \cdot 2\text{H}_2\text{O}$. In the case of the green isomer *V*, the pseudo-octahedral structure requires the existence of a polymeric system, with thiocyanate groups functioning as bridges between the Ni(II) atoms. With regard to the assumed encircling of $\text{NiN}'_2\text{N}''_2\text{S}_2$ in isomer *V* and of $\text{NiN}'_2\text{N}''_2\text{O}_2$ in complexes *I* and *IV*, considerable tetragonal distortion is presumed (N' is the nitrogen atom in the NCS group, N'' is the nitrogen atom of lepidine). In agreement with the results of other authors^{8,9} the two complex absorption bands can be ascribed to the transitions ${}^3B_{1g} \rightarrow {}^3B_{2g}$

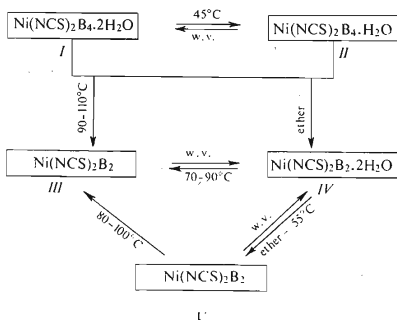


FIG. 1

A Scheme of Mutual Transformations between the Studied Isothiocyanate Nickel(II) Complexes with Lepidine

w.v. water vapour.

and ${}^3B_{1g} \rightarrow {}^3E_g^a(F)$, or ${}^3B_{1g} \rightarrow {}^3E_g^b(F)$ and ${}^3B_{1g} \rightarrow {}^3A_{2g}(F)$ in a weak tetragonal field of symmetry D_{4h} . A similar splitting of the second band is obtained in the spectrum of the green isomer $Ni(NCS)_2(\text{quinoline})_2$ ^{1,4}, and of the pseudo-octahedral complex, $Ni(NCS)_2(\text{thiosemicarbazide})_2$, in the case of which the tetragonal distortion of the basic polyhedron was also verified by X-ray structure analysis¹⁰.

In the spectrum of the red isomer (*III*), a pronounced band with a maximum at 19250 cm^{-1} is located in the region which has been assigned to the first of the three bands in the spectrum of square planar nickel(II) complexes¹¹ (the two other bands are overlapped by the charge-transfer band in the UV region). This is also in agreement with the results of magneto-chemical measurements⁶ ($\mu_{\text{ef}} = 0.56\text{ B.M.}$ at 293 K).

Complex *II* has spectral properties very markedly different from those of the previous pseudo-octahedral or square planar complexes, which are, on the other hand, very similar to those of the complexes with the co-ordination number of five, with trigonal bipyramide structure^{12,13}. On the basis of the above facts, and of the fact that the complexes $[NiX_2L_4]$ ($L = \text{quinoline}$ and its derivatives) cannot be prepared for steric reasons, the composition of the primary coordination sphere of complex *II* $[Ni(NCS)_2B_3]$ is considered to be possibly of trigonal bipyramide structure, with the triplet ground state, ${}^3E'(F)$, of symmetry D_{3h} . This conclusion is also not at variance with the results of magneto-chemical measurements⁶ ($\mu_{\text{ef}} = 3.23\text{ B.M.}$ at 293 K). In agreement with this, the sharp intense band with a maximum at 14500 cm^{-1} can then be ascribed to the transition ${}^3E'(F) \rightarrow {}^3A'_2(F)$, and the band with a maximum at 10700 cm^{-1} to the transition into a state composed of ${}^3A'_1$ and ${}^3A'_2$. The band with a maximum at 20700 cm^{-1} (a shoulder), and the intense band with a maximum at 24600 cm^{-1} , which are connected with transitions to the states ${}^3E''(P)$ and ${}^3A'_2(P)$, are already considerably overlapped by the bands connected with charge-transfer and ligand absorption.

The character of the bonding of the NCS groups and of the water molecules was studied by means of infrared absorption spectra. The valence vibrations of C—N and C—S (the regions 2050 to 2200 cm^{-1} and 700 to 900 cm^{-1}) were especially studied to ascertain the NCS group co-ordination.

As to complex *I*, with regard to the assumed primary co-ordination sphere $[Ni(NCS)_2(H_2O)_2B_2]$, the intense band at 2122 cm^{-1} corresponding to the C—N vibration, can be ascribed to the terminally bonded NCS group. The presence of water in the primary co-ordination sphere apparently causes a shift of this band toward higher wave numbers, as has been stated for M—NCS co-ordination^{14,15}. Also with complex *IV*, a band was observed only at 2125 cm^{-1} , while with complex *II*, in which water is located outside the primary co-ordination sphere, two bands were found below 2100 cm^{-1} . The study of the C—S valence vibration, showed whether there is a bonding through nitrogen or through sulphur. As follows from Table I, splitting of the three intense lepidine bands occurs with complex *I*. This can be

explained either by a change in the overall symmetry of lepidine, or by bonding in two different ways (co-ordinated and non-co-ordinated). With regard to the fact that, with complex *IV*, containing only two lepidine molecules, this band splitting disappears, we prefer the latter alternative. The bands at 805 cm^{-1} and 788 cm^{-1} , which are not observed in the spectrum of free lepidine, can be attributed to co-ordinated water¹⁶, or to $M\text{—NCS}$ co-ordination^{14,15}. Similarly, with complex *IV*, a $C\text{—S}$ vibration band was found at 792 cm^{-1} , which also corresponds to a terminal NCS group bonded through nitrogen. The band at 841 cm^{-1} , which is shifted towards higher wave numbers compared to complex *I*, was identified as corresponding to co-ordinated water. The band for co-ordinated water is generally very sensitive even to changes in the secondary co-ordination sphere¹⁶, by means of which the observed shift can be explained. On careful dehydration, this band disappears and the green isomer *V* with pseudo-octahedral polymeric structure is formed. According to Clark and Williams¹⁷, the molecular symmetry in such a case requires doubling of the $C\text{—N}$ vibration, which was actually found with complex *V* ($\tilde{\nu}_{C\text{—N}}$ at 2121 cm^{-1} with a shoulder at 2136 cm^{-1} , $\tilde{\nu}_{C\text{—S}}$ at 806 cm^{-1} and 791 cm^{-1}). On transition to the red isomer *III*, a decrease of the $C\text{—N}$ vibration to 2100 cm^{-1} occurs, which is in agreement with $\tilde{\nu}_{C\text{—N}}$ for a terminally bonded NCS group. With this complex, considerable changes in the positions and intensities of the co-ordinated lepidine are observed in the $C\text{—S}$ vibration region. Compared to the previous complexes, the band at about 890 cm^{-1} is not observed, but two new bands at 863 and 782 cm^{-1} appear, the first of which is located in the region for square planar complexes of the type^{4,18}, $\text{Ni}(\text{NCS})_2\text{L}_2$ (for $\text{Ni}(\text{NCS})_2(\alpha\text{-picoline})_2 - 856\text{ cm}^{-1}$; $\text{Ni}(\text{NCS})_2(2,6\text{-lutidine})_2 - 862\text{ cm}^{-1}$; $\text{Ni}(\text{NCS})_2(\text{quinoline})_2 - 854\text{ cm}^{-1}$). With isothiocyanate nickel(II) complexes with trigonal bipyramide structure, two bands were found¹² for $C\text{—N}$ vibrations, and one to two bands for $C\text{—S}$ vibrations. Also with complex *II*, two bands at 2097 and 2083 cm^{-1} , or a band at 785 cm^{-1} , were found. There are also changes in the characteristic lepidine bands. Differing from complex *I*, the band splitting, characterizing the differences in the lepidine bonding, is unsymmetrical and also differs in its relative intensity.

Thus it can be concluded that two configurational isomers were also prepared in the case of the complex $\text{Ni}(\text{NCS})_2\text{B}_2$, the first with mononuclear square planar configuration (with singlet ground state $^1A_{1g}$) and terminally bonded NCS groups, the other with tetragonal bipyramidal configuration (with a triplet ground state $^3B_{1g}$) and with bridging NCS groups. Both isomers were prepared by heterogeneous reactions. It seems probable that an important role in the isomer formation is played by the magnitude of the π -bond contribution to the overall bonding system in the complexes. Ligands with delocalized π -bonds appear to lead to such isomerization. The NCS group and quinoline and its derivatives are among such ligands.

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