ISOMERISM OF NICKEL(II) COMPLEXES. III.*

THERMAL DECOMPOSITION OF $Ni(NCS)_2$ (QUINOLINE)$_4$. 2 H_2O
INTO TWO ISOMERS OF $Ni(NCS)_2$ (QUINOLINE)$_2$

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Using TG, DTG, DTA, infrared absorption spectra and powder diffractograms the thermal decomposition of the solid complex $Ni(NCS)_2Q_4$. 2 H_2O (Q = quinoline) was investigated. It was found that the decomposition started with a release of water. It was proved that even under nonisothermal conditions two isomers of $Ni(NCS)_2Q_2$ were formed by thermal decomposition depending on the size of the particle and the thickness of the layer. The complex $Ni(NCS)_2Q_4$ as an intermediate was not observed. Principles and mechanism of the formation of the isomers are discussed.

In spite of the fact that many nickel(II) isomers have been prepared[1], there are no general principles known which would enable a systematic preparation of isomers with a proposed structure. Such principles are, however, known for Pt(II) complexes[2] and they might be expected also for Ni(II) complexes because of the analogous electronic configurations of Ni(II) and Pt(II). Using the principles of transactivity (particularly its kinetics) several isomeric compounds were prepared for substitutionally inert[3] complexes of Pd(II) and Pt(II) also in homogeneous systems. For Ni(II) complexes in solution are often substitutionally unstable our study was aimed at heterogeneous systems namely at their thermal decomposition, in which under suitable conditions also thermodynamically less stable isomers can be prepared.

In this paper the thermal decomposition of the solid complex $Ni(NCS)_2Q_4.2 H_2O$ was followed with respect to the formation of two configuration isomers[1,6] $Ni(NCS)_2Q_2$. The initiative of this study started from the assumption of the existence of several pairs of configuration isomers of $Ni(NCS)_2L_2$, where L is a pyridine derivative[4]. From several types of isomerism we studied the origin of configuration isomers because they are the most typical of nickel(II) complexes[1,5] (in contrast to those of Pd(II) and Pt(II)).

EXPERIMENTAL

Reagents, analytical methods, preparation of the starting complex $Ni(NCS)_2Q_4.2 H_2O$ are described in paper[1,6]. Though this dihydrate can be reproducibly prepared under constant conditions, changes of temperature bring about the formation of crystals of similar appearance but

with different nickel content. The stoichiometric ratio (Ni : Q) ranges in dependence on the temperature ($-20°$ to $30°C$) between 1 : 4·3 (7·55% Ni) and 1 : 3·9 (8·16% Ni). This indicates non-stoichiometric character of this complex. In our further study only the samples with $8·02-8·16\%$ Ni were used. The thermal decomposition of the starting complex was followed with the aid of the derivatograph OD 102 (MOM Budapest). The apparatus is described in paper[7]. Platinum crucibles having 14 mm in diameter in their upper part and Pt, Pt-Rh thermocouples were used for DTA. Measuring conditions: weight of the sample 100 mg, sensitivity for DTA, DTG and TG were 1/3, 1/5 and 100 mg, resp., the rate of the temperature increase $3°C$ min^{-1}. All measurements were carried out under these conditions in air medium. Powder diffractograms were obtained on the powder diffractograph GON (Chirana). Infrared spectra of the solid samples in KBr were obtained on the double-beam spectrophotometer UR-10 (Zeiss, Jena) in the region of $400-4000$ cm^{-1}.

RESULTS AND DISCUSSION

The thermal decomposition of a coarse crystalline (X) and finely ground (Y) complex of $Ni(NCS)_2Q_4.2 H_2O$, Figs 1 and 2, resp., were studied derivatographically. The starting point of this investigation was the possibility of preparing isothermally two $Ni(NCS)_2Q_2$ isomers[1,6] according to the size of the particles (or the thickness of their layer). The thermal decomposition of the starting samples X, Y begins at about $60°C$. In the case of X it proceeds in five steps. As it follows from the DTG curve the second step involves two processes. The losses of mass follow that correspond to the steps for X and Y: 4·5, 40·0, 57·5, 76·7% and 5·7, 40·0, 76·5%, resp. The losses agree satisfactorily with the calculated values $(-2 H_2O$: 4·95%; $-2 H_2O-2 Q$: 40·55%; $-2 H_2O-3 Q$: 58·33%; $-2 H_2O-4 Q$: 76·13%). The maxima of the decomposition rate of the processes occur at the following temperatures: 64, 100, 113, 163, 180, 209°C and 87, 163, 195°C for the samples X and Y, resp. As the DTA curves show, only endothermic processes occur.

Closer study dealt with that part of decomposition the final product of which is $Ni(NCS)_2Q_2$. Information on the structure of the both isomers[1,6] and of the starting complex[1,5,6] obtained by indirect method was employed. It was found that the red isomer shows monomolecular square configuration with the terminal NCS group bonded by nitrogen atom $(\tilde{v}_{C-N} = 2108$ cm^{-1} and $\tilde{v}_{C-S} = 854$ $cm^{-1})$. The green isomer shows hexacoordinated tetragonal-bipyramid structure with two NCS groups coordinated in different ways: as a terminal (bonded by nitrogen atom) and a bridging group $(\tilde{v}_{C-N}$ at 2114 and 2153 cm^{-1}, $\tilde{v}_{C-S}$ at 775 and 750 $cm^{-1})$. In the case of $Ni(NCS)_2Q_4.2 H_2O$ the diffusion reflectance spectrum[1] and the magnetic susceptibility[5] suggest pseudooctahedral configuration. The composition of the coordination shell, however, does not follow from the given data. The absence of the absorption band at $690-730$ cm^{-1}, which corresponds to M–SCN[8,9], indicates that the NCS group is end bonded by nitrogen $(\tilde{v}_{C-N} = 2107$ cm^{-1}, $\tilde{v}_{C-S} = 775$ $cm^{-1})$. The presence of water is confirmed by the broad band at 3404 cm^{-1}, which is located in the region of the stretching vibrations of the OH group[10]. The 825 cm^{-1} band (Fig. 3)

can be explained by the deformation vibration of water molecules that are coordinated. Bands of quinoline at 813, 796 and 746 cm^{-1} are marked in Fig. 3.

In studying the properties of the thermolysis products powder diffractograms, infrared absorption spectra and macroscopic observation were used. *Diffraction records* of sample X at the losses of mass of about 1, 5, and 28% (marked in Fig. 1 with symbols a, b, and c) are in Fig. 4. The starting compound is sensitive to grinding (Fig 4 a, b). When excessive grinding is applied, some intensive bands $(2\vartheta = 43.2°)$ disappear and the others change their intensity $(2\vartheta = 7.2°, 28.5°)$. As the other diffractograms (Figs 4c and d) show the content of the starting compound decreases gradually and the only crystalline product is the red isomer of $Ni(NCS)_2Q_2$. (Its diffraction bands are dashed in Fig. 4d.) The *infrared spectra* of the products show that the bands at 3404 and 825 cm^{-1} disappear. That means that the water is released in the first step of the decomposition. The formation of the red isomer is confirmed by the disappearance of the band $\tilde{v}_{C-S}$ at 775 cm^{-1}, which corresponds to the starting material, and by the appearance of the 854 cm^{-1} band; the band $\tilde{v}_{C-N}$ at 2108 cm^{-1} remained unchanged. *Macroscopic observations* showed that in the first bend (point a, Fig. 1) the surface of the crystals was uniformly, covered with a layer of the red isomer and the inner part
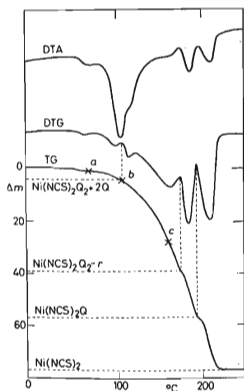

FIG. 1

Derivatogram of the Coarse Crystalline Complex $Ni(NCS)_2Q_4 . 2\ H_2O$

$\varDelta m$ Loss of mass, %; r red.
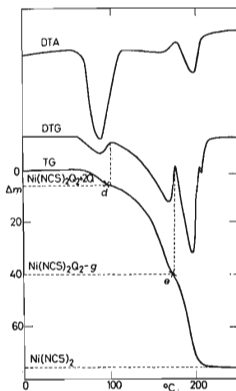
FIG. 2

Derivatogram of the Finely Ground Complex $Ni(NCS)_2Q_4 . 2\ H_2O$

$\varDelta m$ Loss of mass, %; g — green.

of the crystals was not changed. After the second jump (point *b*, Fig. 1) the surface of the crystals was full of cracks and pores in the crystals were dewed with freed quinoline. In the midst of bigger crystals the unconverted starting material could be observed. In point *c* the red isomer was observed only. The remaining quinoline seemed to be adsorbed.

The properties of the products of thermal decomposition of the *Y* sample were studied at 5 and 40% losses of mass marked with *d* and *e* in Fig. 2. The disappearance of the first jump is an important difference suggesting that no compact layer is formed when a powdered sample is treated. Also the two processes connected with the most remarkable endothermic effects on the DTA curve, corresponding to the release of water (and a part of quinoline), are reduced to one process only. The further
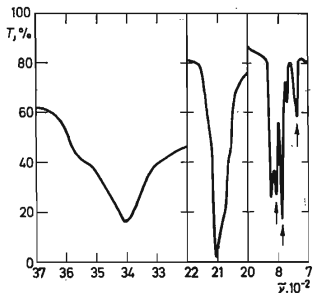

Fig. 3

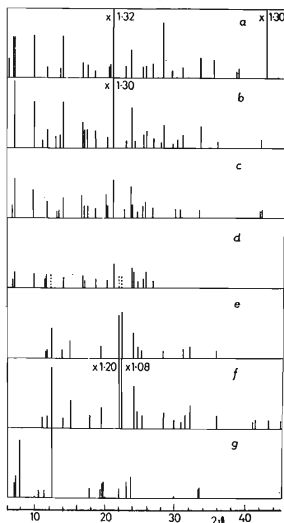Infrared Absorption Spectrum of the Complex $Ni(NCS)_2Q_4.2\,H_2O$


Fig. 4

Powder Diffractograms

a Weakly ground starting material, *b* hardly ground starting material, *c* sample *a*, *d* sample *b*, *e* sample *c*, *f* red isomer of $Ni(NCS)_2Q_2$, *g* green isomer of $Ni(NCS)_2Q_2$.

decomposition in this case is identical with that of sample X except for the formation of the green isomer of $Ni(NCS)_2Q_2$ (Fig. 4g), which contrary to the red isomer decomposes in one step. The small interruption of the DTG curve in the end of the decomposition is brought about by contamination with the red isomer. The bigger the sample is or the higher the layer the more intensive this band is. This was explained by increasing content of the red isomer. The complex $Ni(NCS)_2Q_4$ as a decomposition intermediate of the samples X and Y was not found. After the water release the anhydrous isomers were formed directly. (The remaining quinoline is no part of the complex.)

As the coordination number of Ni(II) in the starting complex equals 6 and as the NCS groups and H_2O are bonded as monofunctional ligands, only two molecules of quinoline may be coordinated. That is why the complex composition should be written as $[Ni(NCS)_2(H_2O)_2Q_2] \sim 2 Q$. Similar results were found by King and co-workers[12]. The remaining quinoline is a part of the crystalline state probably with clatrate structure. This is confirmed by the nonstoichiometric character of the starting complex.

The fact that two volatile ligands (water and quinoline) are present in the primary coordination shell of the initial complex yields the starting point for the derivation of a possible formation mechanism of the two isomers. Decomposition starts with the release of water. This fact combined with the impossibility of coordination of other quinoline molecules due to steric reasons[11] necessitates reorganisation of the structure. Either $Ni(NCS)_2Q_2$ molecules are formed (Scheme 1, A) or the fifth and sixth coordination place are occupied by a new ligand (B). In the latter case the transformation of one terminal NCS group occurs into the bridge bonded group.
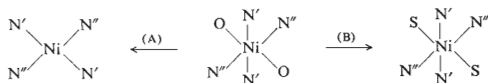
SCHEME 1

It follows from the experiments that in the decomposition of the starting complex there is a potential possibility of the occurrence of the both mentioned processes. The question rises why under certain conditions one isomer is formed only. From the thermodynamical point of view the formation of the more stable red isomer should be expected. However, the kinetics of the isomer formation seems to be the controlling factor. Formation of the red isomer can be observed in the decomposition of rough crystalline material. In this case after the release of water and the decay of the lattice the solution of the corresponding complex in quinoline is formed. The green isomer is formed during the decomposition of finely ground starting material, in which after the water release and the breakdown of the crystal lattice no solution was macroscopically observed and the quinoline is probably adsorbed on a solid reaction pro-

duct. On the basis of this information one may conclude that formation of the liquid phase enables the production of a seed of the thermodynamically more stable red isomer. This was proved by some additional experiments. (By adding quinoline to a sample of *Y* or to the green isomer, or by adding 5% of the red isomer to a sample of *Y* only the red isomer is formed as a result of heating at 100°C.)

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