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# Influence of Ligand Properties on Stereochemistry of Solid Thiocyanate Nickel(II) Complexes with Pyridine Derivatives

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*Stereochemistry of solid complex compounds Ni($NCS)_2(q$-$Rpy)_2$ has been studied in dependence on various positions of a substituent (q = 2, 3, and 4) in pyridine ligand (py), as well as on the nature of substituent (R = Me-methyl, Et-ethyl, $NH_2$, Cl, Br, and CN). The complexes under investigation have shown pseudo-octahedral configurations, with the exception of $Ni(NCS)_2(2$-$Rpy)_2$ (R = Me, Et) which proved by magnetic and spectral measurements to be square-planar. Various positions of alkyl-substituents in the pyridine ligand, and various anionic ligands (X = NCS, Cl, Br, and I) and central atoms (M = Ni, Co, and Cu) are discussed individually in relation to their influence on the stereochemistry of complexes $M^{II}X_2(q$-$Rpy)_2$.*

## Introduction

There are various arrangements of donor atoms around the nickel atom in nickel(II) complexes [1]. Octahedral, square-planar, and tetrahedral configurations are most typical for nickel(II) complexes with pyridine and its derivatives, and when formed, electronic and steric properties of ligands and their mutual interactions play an important role [1, 2].

From this aspect our attention has been paid to complexes $Ni(NCS)_2(q$-$Rpy)_2$ (q = 2, 3, 4; R = Me, Et, $NH_2$, Cl, Br, and CN) because it was expected that a change of the substituent and its position in the pyridine ligand could also cause a change in the stereochemistry of the complexes. The gained knowledge can contribute to preparations of complexes with expected geometry and reactivity [3].

## Experimental

### *Starting Materials*

The liquid pyridine derivatives (Fluka AG or Merck) were distilled under reduced pressure. 4-chlor-pyridine and 4-brom-pyridine were prepared by mixing 0.1 mol 4-Clpy·HCl and 4-Brpy·HCl, with 0.15 mol NaOH in 40 ml $H_2O$. The purity of each sample was checked by infrared spectra.

### *Analysis*

Nickel was determined by EDTA titration; carbon, hydrogen, and nitrogen by microanalysis (Carlo Erba Model 11-02).

### *Physical Measurements*

Magnetic moments were measured with a Gouy balance for the powdered solids at 293 K. Electronic (d–d) spectra of the solid samples in nujol mulls were recorded with a Unicam Model SP 700 C spectrophotometer, and for some of the samples also with a Cary Model 17 spectrophotometer. Infrared absorption spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer (as nujol mulls) and with a UR Model 20 spectrophotometer (as KBr pellets) in the range 4000–400 $cm^{-1}$. Electronic and infrared spectra were measured at room temperature.

### *Preparation of the Complexes*

#### *The Complexes with 2-Rpy*

$Ni(NCS)_2(2$-$Mepy)_2$ was prepared by the previously reported method [4, 5]. $Ni(NCS)_2(2$-$Etpy)_2$, $Ni(NCS)_2(2$-$Brpy)_2$ and $Ni(NCS)_2(2$-$Clpy)_2$ were prepared by the following general method. A saturated, filtered solution of the $Ni(NCS)_2$ in anhydrous ethanol was mixed with an ethanolic solution of the 2-Rpy ligand (the nickel-to-ligand molar ratio was approximately 1:4). The product was washed with ether and dried in a desiccator over $P_2O_5$.

When 2-$NH_2$py was used, a complex with a composition of $Ni(NCS)_2(2$-$NH_2py)_2 \cdot 3/4(C_2H_5)_2O$ could be obtained. The latter compound was prepared after $Ni(NCS)_2(2$-$NH_2py)_4$ had been stirred several times with ether [6]. We have failed in our attempts to prepare pure $Ni(NCS)_2(2$-$NH_2py)_2$.

$Ni(NCS)_2$ when mixed with 2-CNpy in aqueous, methanolic or ethanolic solutions gives a product with a possible composition of $Ni(NCS)_2(2$-$CNpy)_2 \cdot 2ROH$ (R = H, $CH_3$, $C_2H_5$). We did not succeed in removing solvent molecules from the crystalline product, because heating in a vacuum (over 373 K) was always accompanied by decomposition of the complex.

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### *The Complexes with 3-Rpy*

Reactions of ethanolic or aqueous solutions of $Ni(NCS)_2$ with a respective 3-Rpy gave complexes with a composition of $Ni(NCS)_2(3\text{-}Rpy)_4$. Complexes $Ni(NCS)_2(3\text{-}Brpy)_2$, $Ni(NCS)_2(3\text{-}Etpy)_2$ and $Ni(NCS)_2(3\text{-}NH_2py)_2$ could be obtained when ethanolic solutions of 3-Brpy, 3-Etpy, and 3-$NH_2$py respectively were added to the diluted ethanolic $Ni(NCS)_2$ solutions, and nickel-to-ligand molar ratios were in the range 1:1 to 1:2. In preparing the complex with 3-$NH_2$py it was required to add diethylether (about 30%) to the reaction mixture.

Complexes with compositions of $Ni(NCS)_2(3\text{-}CNpy)_2$ and $Ni(NCS)_2(3\text{-}Clpy)_2$ could directly be prepared by thermal decomposition of complexes $Ni(NCS)_2(3\text{-}Rpy)_4$ [7]. However, better results were obtained for the complexes prepared by the following procedure: $Ni(NCS)_2(3\text{-}CNpy)_4$ or $Ni(NCS)_2(3\text{-}Clpy)_4$ were stirred with an excess of $CH_2Cl_2$ for several hours. Solid intermediates obtained in this way, when vacuum-heated at 333 K and 373 K, gave $Ni(NCS)_2(3\text{-}CNpy)_2$ and $Ni(NCS)_2(3\text{-}Clpy)_2$ respectively.

### *The Complexes with 4-Rpy*

$Ni(NCS)_2(4\text{-}CNpy)_2$, $Ni(NCS)_2(4\text{-}Etpy)_2$, and $Ni(NCS)_2(4\text{-}NH_2py)_2$ were prepared by the reaction of diluted ethanolic solutions of $Ni(NCS)_2$ with those of 4-CNpy, 4-Etpy, and 4-$NH_2$py, respectively, the nickel-to-ligand molar ratios being between 1:1 and 1:2.

Complexes with 4-Clpy and 4-Brpy were prepared as follows: A saturated ethanolic $Ni(NCS)_2$ solution was mixed and stirred with the respective ligand in the above nickel-to-ligand molar ratio. At first a blue solid product was precipitated, which contained from three to four molecules of the organic ligand in regard to one nickel atom. However, fine crystalline green products of the composition $Ni(NCS)_2(4\text{-}Rpy)_2$ were obtained after the suspension had been stirred intensively for several hours.

## Results and Discussion

### *The Magnetic and Spectral Properties of the Complexes $Ni(NCS)_2(q\text{-}Rpy)_2$*

The magnetic moments and spectral data are given in Tables I and II. As it is shown there exist two groups of complexes differing in magnetic and spectral properties. The first group includes complexes $Ni(NCS)_2(2\text{-}Rpy)_2$ (R = Me, Et).

The complexes of the first group exhibit small, positive corrected molar susceptibilities ($\chi_M'$). Only one considerably broad and intense band is observed in the measured region of electronic spectra. Consequently, complexes $Ni(NCS)_2(2\text{-}Rpy)_2$ (R = Me, Et) can be considered as being monomolecular square-planar species.

The electronic spectral data and the effective magnetic moments measured for the complexes of the second group are within the region usually found for paramagnetic pseudo-octahedral nickel(II) complexes.

The coordination mode of the ligands was studied by means of infrared spectra. All pseudo-octahedral complexes $Ni(NCS)_2(q\text{-}Rpy)_2$ (for q = 3 and 4 and R = Me, Et, Cl, Br, CN, or for q = 2, R = Cl, Br) show a very strong absorption band (sometimes split) at about 2120 $cm^{-1}$ (Table II). This band ($\nu_{CN}$) is observed for the complexes under study at higher frequencies (25–40 $cm^{-1}$) compared with that registered for monomeric pseudo-octahedral complexes $Ni(NCS)_2(q\text{-}Rpy)_4$. The splitting of the band observed for some complexes can evidently be connected with the non-linearity of SCN–Ni–NCS group, and it is observed for polymeric thiocyanate complexes [8]. The presence of only bidentate bridging NCS groups in these complexes (Fig. 1) is usually also supported by occurrence of two $\delta_{NCS}$ bands [9, 10].

It has been shown for thiocyanate nickel(II) complexes with 2-, 3-, and 4-$NH_2$py [6] that one or both molecules of aminopyridine are coordinated as a bidentate ligand, *i.e.* through the nitrogen atoms of both pyridine ring and amino group. These polymeric complexes also contain NCS groups (one or both) coordinated as monodentate N-bonded ligands.

It has been found however that the complexes prepared with 2-CNpy [11] do not contain 2-CNpy molecules as ligands but addition products of 2-CNpy with solvent molecules (pyridine-2-carboxamide and its N-methyl or N-ethyl derivative). The latter conclusion has been supported by appearance of new bands in the infrared spectra, especially of a very intense band assigned to the amide I in the region of 1653–1665 $cm^{-1}$, whereas the band assigned to the $\nu_{CN}$ vibration of the nitrile group in 2-CNpy did not occur. In these complexes NCS groups are always monodentate N-bonded ligands.

### *Influence of q and R on Stereochemistry of Solid Nickel(II) Complexes $Ni(NCS)_2(q\text{-}Rpy)_2$*

Stereochemistry of complexes $Ni(NCS)_2(q\text{-}Rpy)_2$ in dependence on various positions and nature of the substituents (q and R, respectively) is given in Table I.

For the complexes in which the substituent R = Br, Cl, CN, or $NH_2$, the pseudo-octahedral configuration only was found, regardless of the position of the substituents. Since 2-, 3-, and 4-$NH_2$py behave as polydentate ligands in the above mentioned complexes, and the complex with 2-CNpy ligand does not keep its composition, no discussion will be made on the latter complexes.

The complexes with R = Me, Et in the 4- or 3-position are pseudo-octahedral (polymeric structures

TABLE I. Magnetic Moments, Electronic Spectral Data, and Stereochemistry of Ni(NCS)$_2$(q-Rpy)$_2$ Complexes.

| Complex | $\mu_{eff}$ (B.M.) | Maxima of absorption bands[c] (cm$^{-1}$) | | | Stereo-chemistry[d] |
|---|---|---|---|---|---|
| Ni(NCS)$_2$(2-Mepy)$_2$ | 0.67 | | 19800 | | S |
| Ni(NCS)$_2$(2-Etpy)$_2$ | 0.89 | | 20000 | | S |
| Ni(NCS)$_2$(2-Clpy)$_2$ | 3.34 | 9300 | 15450 | 25500 | O |
| Ni(NCS)$_2$(2-Brpy)$_2$ | 3.31 | 7200<br>10100sh | 14900 | 25600 | O |
| Ni(NCS)$_2$(2-CNpy)$_2$·2H$_2$O[a] | 3.20 | 10500 | 16750 | 25500–27000 | O |
| Ni(NCS)$_2$(2-CNpy)$_2$·2CH$_3$OH[a] | 3.18 | 10800 | 18000<br>16400sh | | O |
| Ni(NCS)$_2$(2-CNpy)$_2$·2C$_2$H$_5$OH[a] | 3.18 | 10950 | 18000<br>16400sh | | O |
| Ni(NCS)$_2$(2-NH$_2$py)$_2$·3/4(C$_2$H$_5$)$_2$O | 3.26 | 9350 | 15050 | 23000–25000 | O |
| Ni(NCS)$_2$(3-Mepy)$_2$[b] | 3.28 | 10000–12000 | 15300br | 28200 | O |
| Ni(NCS)$_2$(3-Etpy)$_2$ | 3.22 | 9200<br>10000sh | 16000 | | O |
| Ni(NCS)$_2$(3-Clpy)$_2$ | 3.28 | 9600 | 15900 | | O |
| Ni(NCS)$_2$(3-Brpy)$_2$ | 3.23 | 8600<br>10700sh | 16000<br>14050sh | | O |
| Ni(NCS)$_2$(3-CNpy)$_2$ | 3.34 | 9600<br>11400sh | 16600 | | O |
| Ni(NCS)$_2$(3-NH$_2$py)$_2$ | 3.21 | 9700 | 16200 | 24500–26500 | O |
| Ni(NCS)$_2$(4-Mepy)$_2$[b] | 3.17 | 10000–12000 | 15500<br>16130 | 28000sh | O |
| Ni(NCS)$_2$(4-Etpy)$_2$ | 3.18 | 8200<br>11100sh | 16450 | | O |
| Ni(NCS)$_2$(4-Clpy)$_2$ | 3.16 | 9700 | 16100 | | O |
| Ni(NCS)$_2$(4-Brpy)$_2$ | 3.22 | 8400<br>11000sh | 16400 | | O |
| Ni(NCS)$_2$(4-CNpy)$_2$ | 3.28 | 9000<br>11200sh | 16500 | | O |
| Ni(NCS)$_2$(4-NH$_2$py)$_2$ | 3.24 | 8400<br>11200sh | 16500 | | O |

[a] Compositions of the complexes are discussed in the text. [b] The values are taken from paper by Nelson *et al.* [19]. [c] sh = shoulder, br = broad. [d] O: octahedral, S: square-planar.

with bidentate NCS groups, Fig. 1, [8, 12]), whereas those with the substituent in the 2-position are square-planar. In elucidating these stereochemical changes it is important to consider different steric and electronic properties of the ligands. The substituent in the 2-position on the pyridine ring shows a steric interaction between R and NCS groups, having as its consequence the destabilization of such a structure. Stabilization can be achieved by the lenghthening of the Ni–N(py) bond or by the twisting of the pyridine ring against the equatorial plane, as is supported by the X-ray structure analysis results for similar complex Ni(NCS)$_2$(2,5-Me$_2$py)$_2$ [13] (Fig. 2). The 2-substituent of the twisted pyridine ring makes the interaction in axial positions more difficult, contrary to substituents in positions 4 or 3 [7, 14], and thus the formation of the pseudo-octahedral complex Ni(NCS)$_2$(2-Rpy)$_2$ is more complicated. In the complexes with 2-Clpy and 2-Brpy, however, pseudo-octahedral configuration is achieved by the sulphur atoms of neighbour thiocyanate groups thus forming a polymeric system (Fig. 1). Although the consequences of different steric properties of the substituents in position 2 cannot be totally excluded (bulky substituents like CH$_3$, C$_2$H$_5$ may show greater steric effects compared with one-atomic substituents Cl or Br), the observed stereochemical changes can be elucidated by different electronic properties of 2-Rpy.

Alkyl substituents exhibit positive inductive effects (+I), and consequently the basicity and $\sigma$-bonding ability of 2-alkyl substituents should have been greater than those of halogeno-pyridines. The order of the base strengths is as follows: 2-Mepy = 2-Etpy > 2-Brpy > 2-Clpy in accordance with p$K_a$ values: 5.97 = 5.97 > 0.90 > 0.72 respectively [15]. The above properties of 2-alkyl-pyridines are sufficient to form stable square-planar, *i.e.* tetra-

TABLE II. Typical Thiocyanate Vibrations ($cm^{-1}$) of Complexes $Ni(NCS)_2(q\text{-}Rpy)_2$.

| q-Rpy | ν(C–N) | ν(C–S)[a] | δ(NCS) |
|---|---|---|---|
| 2-Mepy | 2105 | 856 | 480<br>493 |
| 2-Etpy | 2113 | 851 | 477 |
| 2-Clpy | 2116<br>2134 | 792 | 462br[b] |
| 2-Brpy | 2115<br>2137 | 790 | 460br |
| 2-CNpy(·$2H_2O$) | 2102 | | 467sh<br>472 |
| 2-CNpy(·$2CH_3OH$) | 2091 | 805 | 470 |
| 2-CNpy(·$2C_2H_5OH$) | 2100 | | 458<br>470 |
| 2-$NH_2$py(·$3/4(C_2H_5)_2O$) | 2099<br>2135 | | 475br |
| 3-Mepy | 2120 | | 474<br>481 |
| 3-Etpy | 2114 | 783 | 475br |
| 3-Clpy | 2118 | | 473<br>482 |
| 3-Brpy | 2107<br>2127sh[b] | | 470<br>478 |
| 3-CNpy | 2127 | | 466<br>477 |
| 3-$NH_2$py | 2095<br>2119 | | 462<br>478<br>483 |
| 4-Mepy[c] | 2122 | 785 | 458<br>468 |
| 4-Etpy | 2120 | | 468<br>475 |
| 4-Clpy | 2114<br>2123 | 786 | 475br |
| 4-Brpy | 2116 | 782 | 466<br>475 |
| 4-CNpy | 2126 | 780 | 460sh<br>470 |
| 4-$NH_2$py | 2110 | 790 | 473sh<br>483 |

[a] Very often is overlapped by ligand absorption. [b] sh = shoulder, br = broad. [c] The values are taken from ref. [12].

coordinated Ni(II) complexes. Halogeno substituents show negative inductive effects (–I), and thus a considerably lower electronic density occurs on N(py) which requires a formation of hexa-coordinated, although less stable Ni(II) complexes.

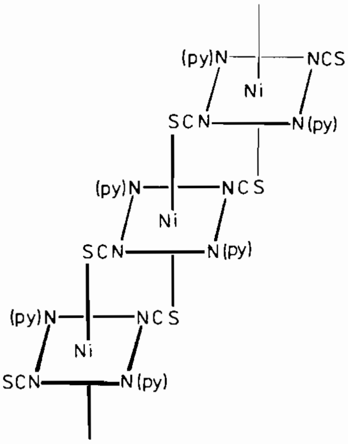

Fig. 1. The structure suggested for the pseudo-octahedral complexes of the type $Ni(NCS)_2(q\text{-}Rpy)_2$ [8, 12].

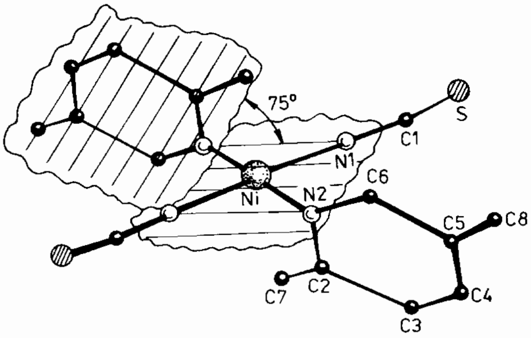

Fig. 2. The position of 2,5-$Me_2$py in relation to the plane $NiN_4$ [13].

The importance of the electronic properties of 2-Rpy in relation to the stereochemistry of complexes $Ni(NCS)_2(2\text{-}Rpy)_2$ is emphasized, for instance, by comparison with the complexes of 3-methylisoquinoline. The latter ligand when compared with 2-Mepy shows analogical steric properties but a lower basicity. It also forms a square-planar and moreover, pseudo-octahedral isomeric complexes $Ni(NCS)_2$(3-methylisoquinoline$)_2$ [16].

The explanation for the preferring of a certain configuration in Ni(II) complexes with pyridine derivatives without steric hindrances (q = 3 and 4) is a simpler problem. The changes in the electronic properties of ligands R-py caused by various substituents (R = Cl, Br, CN, Me, and Et) do not make it possible to form complexes other than pseudo-octahedral polymeric $Ni(NCS)_2(q\text{-}Rpy)_2$.

### *Consequences of Mutual Interactions of Ligands on Stereochemistry of Complexes $M^{II}X_2(Rpy)_2$*

The observed stereochemistry of the complexes is a result of several factors (not only effects of Rpy), and is connected with the mutual interactions of ligands in the complexes under study [1, 2]. In order to judge the role of an anionic ligand or the influence of the central atom on the stereochemisty of complexes $M^{II}X_2(Rpy)_2$, attention was paid to the complexes with X = NCS, Cl, Br, I, for Co, Ni, Cu, and R = Me, because the above complexes were prepared with nearly all mono- or di-methyl substituted pyridines.

### *The Anionic Ligand is Changed (M = Ni, R = Me)*

According to the positions of the substituents on the pyridine ring, the complexes can be divided into two groups which differ significantly in their stereochemistry [2, 3, 7, 14, 17, 18]:

First group: Complexes $NiX_2(q\text{-}Rpy)_2$ (q = 4 and 3)

| X | I | Br | Cl | NCS |
|---|---|---|---|---|
| Stereochemistry | T | O | O | O |

Second group: Complexes $NiX_2(q\text{-}Rpy)_2$ (q = 2)

| X | I | Br | Cl | NCS |
|---|---|---|---|---|
| Stereochemistry | S | T | T | S |

T: tetrahedral, O: octahedral, S: square-planar

Owing to an assumed π-acceptor ability to the NCS group [19], the absence of steric hindrances caused by Rpy molecules and the general tendency of the central atom Ni(II) to form hexa-coordinated complexes, the crystalline thiocyanate complexes of the first group exhibit a polymeric octahedral structure. Anionic ligands $Cl^-$ and $Br^-$, being of a smaller size and showing a tendency to form bridges, also give polymeric octahedral complexes. On the other hand iodide anion, due to its polarizability and greater size, requires the formation of complexes with a lower coordination number. Consequently, solid complexes of a type $NiI_2(Rpy)_2$ are tetrahedral.

Due to the steric properties of 2-Rpy ligands, all complexes of the second group exhibit the coordination number four. Considering a relatively strong ligand field of NCS group contrary to a weaker ligand field of anion $Cl^-$ and $Br^-$, it is not surprising that the square-planar configuration is preferred in $Ni(NCS)_2(2\text{-}Rpy)_2$, whereas complexes $NiCl_2(2\text{-}Rpy)_2$ and $NiBr_2(2\text{-}Rpy)_2$ are tetrahedral. The square-planar configuration of $NiI_2(2\text{-}Rpy)_2$ seems to be connected [20] with lattice effects as well as with a higher degree of steric hindrances between 2-Rpy and $I^-$ ligands. When formed, the square-planar configuration allows the plane of the 2-substituted pyridines to twist from the plane of donor atoms, and thus the mutual repulsion of the ligands is lowered.

### *The Central Atom is Changing (X = NCS, R = Me)*

In estimating the part played by the central atom in mutual interactions of ligands the stereochemistry of analogous complexes $M^{II}(NCS)_2L_2$ where M = Co, Ni, Cu; L = py, Mepy, and $Me_2py$, was compared (Table III). The comparison has shown that unlike Ni(II) complexes, the analogous Cu(II) complexes mostly exhibit [21] a pseudo-octahedral configuration while Co(II) complexes [22] have a tetrahedral or octahedral configuration. These results indicate that the determining factor in the mutual interactions of ligands leading to a stabilization of octahedral or square-planar configuration in the Ni(II) complexes are ligand interactions *via* the central atoms [23].

TABLE III. Stereochemistry of Complexes $M^{II}(NCS)_2L_2$.[a]

| L | M | | |
|---|---|---|---|
| | Co [22] | Ni [2] | Cu [21] |
| 2-Mepy | T | S | O |
| 2,3-$Me_2$py | T | | P |
| 2,4-$Me_2$py | T | S | O |
| 2,5-$Me_2$py | T | S | O |
| 2,6-$Me_2$py | | S | O |
| py | O | O | O |
| 4-Mepy | O | O | O |
| 3-Mepy | T | O | O |
| 3,4-$Me_2$py | T | O | O |
| 3,5-$Me_2$py | O | O | O |

[a] T: tetrahedral, S: square-planar, O: octahedral configuration, P: penta-coordinated complex.

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