

# Reaction of distortion isomers of dithiocyanato-bis(pyridine)copper(II) with pyridine

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Received 29 May 1975

Reactions of  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> with pyridine are described. The conditions are specified under which a pair of modifications of Cu(py)<sub>4</sub>(NCS)<sub>2</sub> complex is prepared by reactions of  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> with pyridine as well as the conditions under which these reactions give rise to products with composition Cu(py)<sub>4</sub>(NCS)<sub>2</sub> having the same physicochemical properties. The properties of prepared compounds were studied by thermal methods. Some properties of intermediate products of thermal decomposition of  $\alpha$ - and  $\beta$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub> are also described. The differences between properties of prepared modifications suggest the presence of fine structural differences analogous to those observed for  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub>.

Описаны реакции  $\alpha$  и  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> с пиридином. Дана спецификация условий реакций  $\alpha$  и  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> с пиридином, при которых были приготовлены две модификации комплекса Cu(py)<sub>4</sub>(NCS)<sub>2</sub> и условия реакций  $\alpha$ - и  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> с пиридином, при которых образуются продукты состава Cu(py)<sub>4</sub>(NCS)<sub>2</sub> с одинаковыми физико-химическими свойствами. Свойства приготовленных веществ изучали при помощи термических методов. В работе описаны некоторые свойства промежуточных продуктов термического разложения  $\alpha$ - и  $\beta$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub>. Характер различных свойств, приготовленных модификаций, свидетельствует об аналогии тонких структурных различий, которые наблюдались в  $\alpha$ - и  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub>.

In the study of distortion isomerism of Cu(II) coordination compounds [1] it was found that structural differences between  $\alpha$  and  $\beta$  isomers of Cu(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub> are connected with different degree of distortion of coordination polyhedron around Cu(II) and with changes of geometry of thiocyanato groups [2]. From the studies of infrared spectra, diffraction and thermal properties of  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> complexes and from the knowledge of crystal structure of one form it follows that in this case structural differences analogous to those discovered in isomers of Cu(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub> [3] are involved. However,  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> isomers differ from  $\alpha$  and  $\beta$  isomers of Cu(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub> while no transitions between them have been thus far observed [4]. The aim of this work was to establish whether the structural differences between  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> are retained at chemical reaction with pyridine.

## Experimental

### *Preparation of the complexes*

Complexes with composition Cu(py)<sub>4</sub>(NCS)<sub>2</sub> were prepared by reaction of  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub>, respectively with excess amount of liquid or gaseous pyridine. Isomers of Cu(py)<sub>2</sub>(NCS)<sub>2</sub> were prepared

by the method reported elsewhere [3]. By dissolving  $\alpha$  and  $\beta$  isomers of  $\text{Cu}(\text{py})_2(\text{NCS})_2$  in pyridine at  $\sim 50^\circ\text{C}$  a clear solution was obtained from which dark-green crystals with composition  $\text{Cu}(\text{py})_4(\text{NCS})_2$  denoted as preparates *I* and *II* crystallized at room temperature. Complexes with the same composition were also prepared by the action of pyridine vapour on  $\alpha$ - and  $\beta$ - $\text{Cu}(\text{py})_2(\text{NCS})_2$ , respectively, in a closed space at room temperature. The prepared complexes were denoted as preparates *III* and *IV*. Since the stability of complexes of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  at room temperature is very low, these complexes were studied indirectly by thermal decomposition method.

### *Chemical composition of the prepared complexes*

For  $\text{Cu}(\text{py})_4(\text{NCS})_2$  calculated: 12.80% Cu, 12.92% S, 63.80% py; found: *I*. 12.50% Cu, 12.53% S, 63.95% py; *II*. 12.90% Cu, 12.75% S, 64.10% py; *III*. 12.90% Cu, 12.80% S, 63.70% py; *IV* 12.67% Cu, 12.89% S, 63.75% py.

The copper content was determined complexometrically, the sulfur content was determined as  $\text{BaSO}_4$  after alkaline oxidation melting of samples. The pyridine content was determined by titration (dimethyl yellow + methylene blue) after being released by KOH and absorbed in  $\text{H}_2\text{SO}_4$  solution. The content of nitrogen and carbon in intermediate products was determined by the elemental organic analysis.

### *Instruments*

Thermal decomposition of the complexes was carried out using a OD-102 Derivatograph in temperature range 20 to  $300^\circ\text{C}$  in air at a heating rate  $5^\circ\text{C}/\text{min}$  and the same sample weight 100 mg. Annealed  $\text{Al}_2\text{O}_3$  was used as a standard.

The infrared spectra of intermediate products of thermal decomposition in Nujol were recorded on a UR-20 (Zeiss, Jena) instrument in the range 700 to  $2500\text{ cm}^{-1}$ .

Powder X-ray diffractograms were obtained using X-ray goniometer GON 03 with  $\text{CuK}_\alpha$  radiation and Ni filter. Only the intermediate products of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complexes were studied by diffraction method, because radiation decomposes the studied complexes.

### *Some physicochemical properties of the preparates obtained by thermal decomposition of $\text{Cu}(\text{py})_4(\text{NCS})_2$ complexes*

Two observed types of the thermograms obtained at the thermal decomposition of the prepared  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complexes are shown in Fig. 1. The course of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complexes denoted as preparates *I*, *II*, and *IV* is the same for these complexes up to  $300^\circ\text{C}$  but differs from the course of thermal decomposition of preparate *III*.

Since significant differences in the discussed course of thermal decomposition occur at about  $200^\circ\text{C}$ , the properties of intermediate products of thermal decomposition were studied in this temperature region.

In agreement with thermogravimetric data the following compounds were prepared and studied:

Intermediate products denoted as *M(I)*, *M(II)*, and *M(IV)* were prepared by a 64 weight % degradation of preparates *I*, *II*, and *IV* of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complex at  $185^\circ\text{C}$ . The intermediate product *M(III)* was prepared by a 66 weight % degradation of preparate *III* of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complex at  $220^\circ\text{C}$ . The intermediate products were prepared by decomposition in air.

From analytical evaluation (Table 1) of the intermediate products *M(I)*, *M(II)*, and *M(IV)* it follows that those are substances with a summary formula  $\text{CuN}_2\text{C}_2\text{S}_2$  which are formed by liberation of all

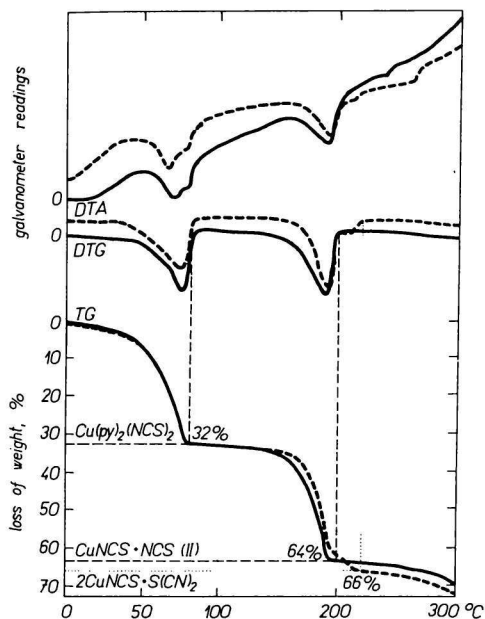


Fig. 1. Thermograms of  $\alpha$ - and  $\beta$ - $\text{Cu}(\text{py})_4(\text{NCS})_2$ .  
 - - -  $\alpha$  form ; —  $\beta$  form.

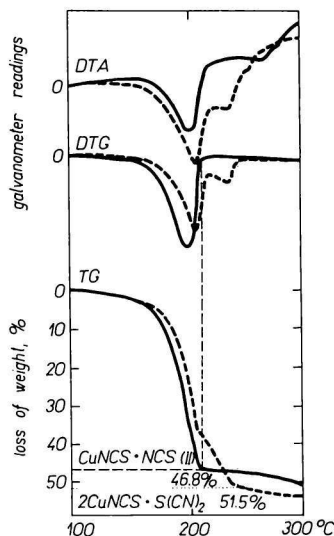


Fig. 2. Thermograms of  $\alpha$ - and  $\beta$ - $\text{Cu}(\text{py})_2(\text{NCS})_2$ .  
 - - -  $\alpha$  form ; —  $\beta$  form.

pyridine molecules from the initial  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complex. At the preparation of intermediate product  $M(III)$  from the initial  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complex not only four pyridine molecules but also a part of sulfur atoms from thiocyanato groups is liberated.

From a comparison of positions of infrared absorption bands, colour, and positions of diffractions in powder X-ray diffractograms (Tables 2—4) it follows that the intermediate products  $M(I)$ ,  $M(II)$ , and  $M(IV)$  have the same physicochemical properties and they differ from the intermediate product  $M(III)$ . At the same time these intermediates closely resemble the red-brown compound  $\text{CuNCS} \cdot \text{NCS}$  described by Hunter *et al.* [5] and they are identical with the products of thermal decomposition of  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  complex [3]. With respect to this analogy the starting  $\text{Cu}(\text{py})_2(\text{NCS})_2$  complexes were conventionally denoted as  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$ .

Table 1

Chemical composition of the intermediate products of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$

Intermediate product	Analytical composition				Atomic ratio			
	% Cu	% S	% N	% C	Cu	S	H	C
$M(I)$	35.48	35.22	15.80	13.66	1	1.97	2.02	2.03
$M(II)$	35.12	35.08	15.84	13.18	1	1.98	2.04	1.98
$M(III)$	38.10	30.18	16.85	14.94	1	1.56	2.02	2.07
$M(IV)$	34.98	34.72	15.91	13.65	1	1.97	2.07	2.07

Table 2

Colour and results of reaction of the intermediate products of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  with conc.  $\text{HNO}_3$

Substance	Colour	Reaction with conc. $\text{HNO}_3$
$\text{CuNCS}^a$	White	Blue solution
$\text{Cu}(\text{NCS})_2$	Black-brown	Blue solution
$\text{CuNCS} \cdot \text{NCS}^a$	Red-brown	Blue solution + yellow insoluble residue
$(\text{NCS})_x^b$	Yellow	Insoluble
<i>Intermediate</i>		
$\text{M}(I)$	Red-brown	Blue solution + yellow insoluble residue
$\text{M}(II)$	Red-brown	Blue solution + yellow insoluble residue
$\text{M}(III)$	Light yellow-brown	Blue solution + yellow insoluble residue
$\text{M}(IV)$	Red-brown	Blue solution + yellow insoluble residue

a) Ref. [5]; b) [6].

Table 3

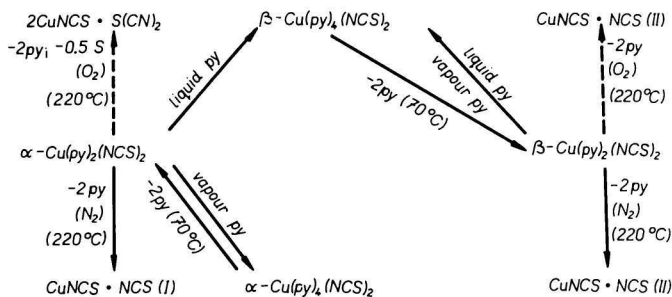
Wavenumbers of absorption bands in infrared spectra of the intermediate products of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  and some standard substances

Substance	Wavenumbers of absorption bands, $\text{cm}^{-1}$		
	$\bar{\nu}(\text{CN})$	$\bar{\nu}(\text{CS})$	$\bar{\nu}(\text{NCS})_x$
$\text{CuNCS}^a$	2170	746	
$\text{Cu}(\text{NCS})_2^a$	2150, 2100	800, 725	
$\text{CuNCS} \cdot \text{NCS}^a$	2180, 2160	755	1270—1130, 930
$(\text{NCS})_x^b$			1270—1130, 930
<i>Intermediate</i>			
$\text{M}(I)$	2180, 2160	755	1270—1130, 930
$\text{M}(II)$	2180, 2160	755	1270—1130, 930
$\text{M}(III)$	2180	755	1270—1130, 930
$\text{M}(IV)$	2180, 2160	755	1270—1130, 930

a) Ref. [5]; b) ref. [6].

The positions of main diffraction lines of the intermediate product  $\text{M}(III)$  with a summary formula  $\text{CuS}_{1.5}(\text{CN})_2$  are conspicuously close to those of  $\text{Cu}(I)$  thiocyanate. Reaction with conc.  $\text{HNO}_3$  as well as the infrared spectra clearly indicate the presence of a polymer thiocyanato group which was only poorly registered in diffractograms. Chemism of polymerization of the thiocyanato group in  $\text{Cu}(I)$  thiocyanate

lattice is apparently different in the discussed case of the  $M(III)$  intermediate from that observed for the above-discussed intermediates  $M(I)$ ,  $M(II)$ , and  $M(IV)$ . Different ways of polymerization of the thiocyanato group in the course of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complexes realized at the same conditions indicate certain structural differences among the initial prepares.



*Scheme 1*

Illustration of mutual transformations of  $\alpha$  and  $\beta$  forms of dithiocyanato-*bis*- and *tetrakis*(pyridine)copper(II) complex.

The properties of  $M(III)$  intermediate are analogous to those of the substance obtained by thermal decomposition of  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2$  complex [3]. (Some very small discrepancies such as absence of some weak diffractions in powder X-ray patterns or absence of splitting of the  $\bar{\nu}(\text{CN})$  absorption band in infrared spectra are probably caused by a more complete polymerization of the thiocyanato groups in the studied sample.) With respect to the above analogies with  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2$  we have conventionally denoted the starting prepare *III* of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  complex as  $\alpha\text{-Cu}(\text{py})_4(\text{NCS})_2$ .

The mutual relations among individual forms of  $\text{Cu}(\text{py})_2(\text{NCS})_2$  and  $\text{Cu}(\text{py})_4(\text{NCS})_2$  ensuing from the laboratory methods of preparation and from the study of prepared complexes by DTA can be summarized in Scheme 1. To individual transformations the following comments can be made:

From  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  up to  $\sim 220^\circ\text{C}$  in nitrogen atmosphere or in air two molecules of pyridine are released and the intermediate products with chemical composition  $\text{CuNCS} \cdot \text{NCS}$  (conventionally denoted as *II*), for more details see [3]) result. These products have the same physicochemical properties regardless of the atmosphere (air or nitrogen) in which the decomposition has been carried out.

From  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2$  up to  $\sim 220^\circ\text{C}$  in a nitrogen atmosphere two molecules of pyridine are released and the intermediate product with chemical composition  $\text{CuNCS} \cdot \text{NCS}$  conventionally denoted as *I*), having physicochemical properties different from those of  $\text{CuNCS} \cdot \text{NCS}$  prepare *II*) results [3].

Complex  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2$  releases in air up to  $\sim 220^\circ\text{C}$  two molecules of pyridine and a part of its sulfur atoms. Composition of the intermediate product corresponds to  $\text{CuS}_{1.5}(\text{CN})_2$  or  $2\text{CuNCS} \cdot \text{S}(\text{CN})_2$ .

Only  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$  complex crystallizes from pyridine solutions of  $\alpha$ - and  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$ . Reaction of pyridine vapour with  $\alpha$ - and  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  gives rise to prepares with different properties denoted as  $\alpha$ - and  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$ .

Procedure:  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2 \xrightarrow{\text{liquid py}} \beta\text{-Cu}(\text{py})_4(\text{NCS})_2 \xrightarrow{-2\text{py}} \beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  represents a possible way of transformation of  $\alpha\text{-Cu}(\text{py})_2(\text{NCS})_2$  to  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  by a chemical reaction.

## Results and discussion

By a reaction of distortion isomers  $\alpha$ - and  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$  with pyridine the complexes  $\text{Cu}(\text{py})_4(\text{NCS})_2$  were prepared. If complexes are prepared by a reaction with pyridine

Table 4

Values of diffraction angles  $2\theta$  of the intermediate products of thermal decomposition of  $\text{Cu}(\text{py})_4(\text{NCS})_2$  and standard substances

Values of diffraction angles $2\theta$ in degrees						
$\text{Cu}(\text{NCS})_2^a$	$\text{CuNCS} \cdot \text{NCS}^a$	Intermed. M(I)	Intermed. M(II)	Intermed. M(IV)	Intermed. M(III)	$\text{CuNCS}^a$
14.9						
16.1	16.1	16.1	16.1	16.1	16.1	16.1
17.4						
20.8		(20.5)	(20.5)	(20.5)		
23.9	24.3	24.3	24.3	24.3	(24.5)	
27.2	27.2	27.2	27.2	27.2	27.2	27.2
27.9						
29.2	29.1	29.1	29.1	29.1	29.1	
30.5	30.5	30.5	30.5	30.5		
31.3		(31.1)	(31.1)	(31.1)		
32.6	32.6	32.6	32.6	32.6	32.6	32.6
33.7						
34.6	34.6	34.6	34.6	34.6	34.6	34.6
35.7						
36.4						
37.6	37.3	37.3	37.3	37.3		
		38.5	38.5	38.5		
42.3						
		43.2	43.2	43.2		
46.7						
47.2	47.2	47.2	47.2	47.2	47.2	47.2
		48.8	48.8	48.8		
50.1	50.1	50.1	50.1	50.1	50.1	50.1

a) Ref. [5].

Note: Diffractions with negligible small intensity are in brackets.

vapour, they show significant differences in the course of thermal decomposition (Fig. 1). Both forms up to  $\sim 250^\circ\text{C}$  liberate all coordinated molecules of pyridine, these being released at chosen conditions in two steps. The course of liberation of the first two molecules of pyridine is the same for both  $\alpha$  and  $\beta$  forms and is characterized by a 32% decrease in mass on the TG curve and by a sharp endothermic minimum at  $\sim 70^\circ\text{C}$  on the DTA curve.

Liberation of the second pair of pyridine molecules from  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$  is registered by a 64% decrease in mass on the TG curve and by another endothermic minimum at  $\sim 185^\circ\text{C}$  on the DTA curve. From the thermograms obtained (Figs. 1 and 2) it follows that the course of thermal decomposition in corresponding region is the same for  $\beta\text{-Cu}(\text{py})_4(\text{NCS})_2$  and  $\beta\text{-Cu}(\text{py})_2(\text{NCS})_2$ .

Liberation of the second pair of pyridine molecules from  $\alpha\text{-Cu}(\text{py})_4(\text{NCS})_2$  (at temperature  $\sim 210^\circ\text{C}$ ) is accompanied by a partial liberation of sulfur atoms from the thiocyanato groups. Similar changes of the thiocyanato groups connected with the partial release of

sulfur atoms were observed by *Batsanov et al.* [7] when Cu(I) thiocyanate was heated up to 440°C. Partial liberation of the sulfur atoms can be considered as a process accompanying and characterizing certain course of polymerization of the thiocyanato groups which was observed only for  $\alpha$  forms.

This secondary process described is significantly registered on the TG and DTG curves and by a small endothermic minimum also on the DTA curve. From a comparison of Figs. 1 and 2 it follows that the course of thermal decomposition in corresponding regions is the same for  $\alpha$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub> and  $\alpha$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub>.

Different courses of thermal decomposition of  $\alpha$ - and  $\beta$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub> and different physicochemical properties of the intermediate products of thermal decomposition indicate different structural properties of the starting complexes. Since the differences between  $\alpha$ - and  $\beta$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub> and  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> found by thermal decomposition are very similar, it can be expected that the structural differences between the discussed pairs of substances are also very similar. From the above mentioned it also follows that the existing structural differences between  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> were not strongly influenced by the chemical reaction with pyridine vapour giving rise to  $\alpha$ - and  $\beta$ -Cu(py)<sub>4</sub>(NCS)<sub>2</sub> complexes. On the other hand, by a reaction of  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> with liquid pyridine Cu(py)<sub>4</sub>(NCS)<sub>2</sub> complexes having the same properties are obtained.

Electronic spectra of all preparates of Cu(py)<sub>4</sub>(NCS)<sub>2</sub> (measured in Nujol suspension) show a relatively broad band of  $d-d$  transition with  $\bar{\nu}_{\max}$  at 14 600 cm<sup>-1</sup> and the same shape for all preparates. This band is apparently shifted if compared with the position of band of the ligand field of Cu(py)<sub>2</sub>(NCS)<sub>2</sub> (15 700 cm<sup>-1</sup>). On this basis the conclusion can be made that at the reaction of pyridine vapour with  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> as well as at the reaction in liquid pyridine two additional pyridine molecules are coordinated in the same manner.

Different choice of conditions for reaction of distortion isomers of Cu(py)<sub>2</sub>(NCS)<sub>2</sub> with pyridine showed that structural differences between  $\alpha$ - and  $\beta$ -Cu(py)<sub>2</sub>(NCS)<sub>2</sub> are preserved even when a partial chemical change in the coordination sphere takes place but the initial crystal structure is not totally destructed. On the contrary, at the reaction in liquid pyridine when more drastic changes of inner coordination sphere can occur in connection with dissolution of Cu(py)<sub>2</sub>(NCS)<sub>2</sub> and crystallization of Cu(py)<sub>4</sub>(NCS)<sub>2</sub> no structural differences between prepared complexes were observed.

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Translated by K. Sarka