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THERMAL PROPERTIES OF THIOCYANATOCOPPER(II) COMPLEXES WITH PICOLINES AND LUTIDINES

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The thermal properties of coordination compounds of the composition $Cu(NCS)_2L_2$ (where $L =$ pyridine, 2-, 3- and 4-picoline, and 2,3-, 2,4-, 2,5-, 2,6-, 3,4-and 3,5-lutidine) are dealt with. The thermal decomposition of these compounds begins with the release of the ligand L. The compounds with pyridine derivatives containing a methyl substituent at position 2 show a markedly decreased initial decomposition temperature. It was found that X-ray irradiation caused a reduction of the central atom Cu(II) in the coordination compounds under investigation. X-ray electron spectra data showed the stability of the compounds $Cu(NCS)_2L_2$ with $L =$ picoline or lutidine having a methyl substituent at position 2 to be distinctly lower in the surface layers. From the given series, the compounds $Cu(NCS)_2(pyridine)_2$ and $Cu(NCS)_2(3,5\text{-lutidine})_2$ exhibit an analogous course of thermal decomposition in nitrogen atmosphere up to 600°. The stoichiometries of thermal decomposition are discussed.

Our former papers [1, 2] dealt with the physico-chemical properties of a series of thiocyanatocopper(II) compounds of the composition $Cu(NCS)_2L_2$, where L meant pyridine and all the isomeric forms of picolines and lutidines. A more detailed analysis of electron and infrared spectra showed the effect of the methyl substituents on the physico-chemical properties of the complexes.

In the series of compunds $Cu(NCS)_2L_2$ (compared with the compound $Cu(NCS)_2(py)_2$) the methyl substituents increase the tetragonal distortion of the coordination polyhedra [1]. Due to the high plasticity [3, 4] of the coordination sphere of Cu(II), the coordination number of 6 remains unchanged in all the compounds except $Cu(NCS)_2(2,3\text{-lut})_2$. This compound exhibited a decrease of the coordination number of the central atom to 5.

A study of the infrared spectra [2] of this compound series showed that the methyl substituents affect the strength of the bond coordinating the pyridine ligand to the central atom. These changes do not remain isolated in the coordination sphere of the central atom, but also induce changes in the bond strength of the coordinated NCS groups.

The aim of this work was to investigate the decompositions of these compounds of type $Cu(NCS)_2L_2$.

Experimental

Preparation of the compounds

Thiocyanatocopper(II) compounds of the general formula $Cu(NCS)_2L_2$ (where L = all the isomeric forms of picolines and lutidines) were prepared and analytically evaluated by the methods described in [1]. α-$Cu(NCS)_2(py)_2$ was also prepared according to [5].

Apparatus

The thermal decomposition of the compunds was performed with a derivatograph (MOM, Hungary) [6]. A platinum crucible 14 mm in diameter and a Pt/Pt–Rh thermocouple were used. All samples were pulverized, the grain-size not exceeding 0.06 mm. The sample weight was 100 mg, and the temperature interval 20 to 600°, with a heating rate of 9°/min. The measurements were made in a nitrogen atmosphere.

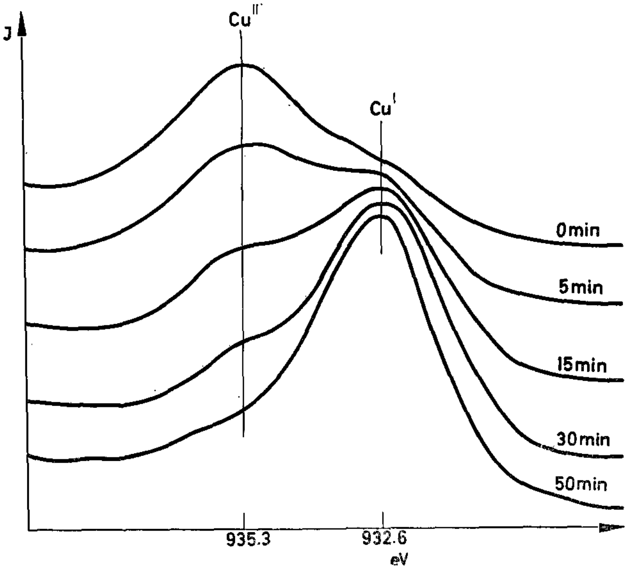

Fig. 1. Change of the line $Cu2p_{3/2}$ in dependence on the radiation time

The influence of X-ray radiation was studied by means of the $Cu^2p_{3/2}$ line of these compounds on a VII–E–15 X-ray electron spectrometer. The spectra were excited by the $Mg_{K\alpha}$ line at 10^{-6} torr. Figure 1 shows the data of the $Cu^2p_{3/2}$ line measured during radiation of $Cu(NCS)_2(3,5\text{-lut})_2$. Figure 2 presents the kinetic data on the change of the signal intensity of Cu(II). Irradiation of the samples was performed with the X-ray tube anode of the spectrometer at 9 kV and 120 mA.

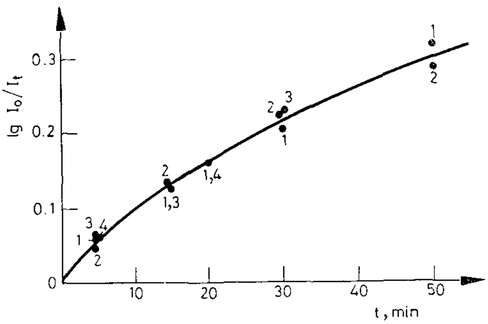

Fig. 2. Change of the intensity I of the line Cu(II)2 $p_{3/2}$ in dependence on the radiation time (1 — L = 3, 5-lut, 2 — L = 3,4-lut, 3 — L = 4-pic, 4 — L = 2-pic)

Results and discussion

The study of the thermal behaviour of thiocyanatocopper(II) coordination compounds of the composition $Cu(NCS)_2L_2$ (where L = 2-, 3- and 4-picoline, and 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-lutidine) showed, compared with $(CuNCS)_2(py)_2$, that the methyl substituents markedly influence the course of the thermal decomposition and lower the thermal stability.

The thermal decomposition of all the above compounds begins with the release of the heterocyclic base. For $Cu(NCS)_2(py)_2$ this is in agreement with the results of Erdey and Liptay [7]; however, they studied the thermal decomposition of this compound in the presence of oxygen.

The fact that the thermal decomposition of all the compounds under investigation begins with the breaking of the Cu – L bonds is in good agreement with the information obtained from the infrared absorption spectra [2]. The wavenumbers of the Cu – L valence vibrations are $\approx 60\ cm^{-1}$ lower than those of the Cu – NCS valence vibrations.

The compounds begin to decompose in the temperature range 70 – 120°. According to their initial decomposition temperature they may be divided into two groups.

The first group involves the compounds with 3-, 4- and 5-substituted pyridine (L = 3-pic, 4-pic, 3,4-lut and 3,5-lut) and unsubstituted pyridine. The thermal decompositions of these compounds commence at 110 – 120°.

The other group covers compounds containing a substituent at the sterically disadvantageous positions 2 or 6. (L = 2-pic, 2,3-lut, 2,4-lut, 2,5-lut and 2,6-lut.) These compounds begin to decompose at a significantly lower temperature, 70 – 80°.

This experimental finding is also in good agreement with the results obtained from the infrared absorption spectra. For all the compounds where *L* has a methyl substituent at position 2, a shift of the Cu – L valence vibration to lower energies was observed compared with compunds where *L* means pyridine (see Table 1).

It was found that X-ray radiation caused a reduction of the central atom Cu(II) in $Cu(NCS)_2L_2$. For $Cu(NCS)_2L_2$ where L = picoline or lutidine with a 2-methyl substituent, even at the beginning of the measurements the X-ray spectra registered an intense signal from Cu(I) and a weak signal from Cu(II). The ratio of the intensities was 5 : 1.

This indicates that, for this series of compounds, nearly complete reduction of the Cu(II) took place on their surface even during storage. This reduction continued as a consequence of X-ray irradiation.

Table 1

Wawe numbers of the valence vibrations $\bar{\nu}(Cu-L)$ and the initial decomposition temperatures of the compounds $Cu(NCS)_2L_2$ (L = py, 2-pic, 2,3-lut, 2,4-lut, 2,5-lut and 2,6-lut)

Compound	Initial decomposition temperature, °C	Wawe number of the valence vibration $\bar{\nu}$ (Cu-L), cm^{-1}
$Cu(NCS)_2(py)_2$	110	257
$Cu(NCS)_2$(2-pic)$_2$	70	242
$Cu(NCS)_2$(2,3-lut)$_2$	80	244
$Cu(NCS)_2$(2,4-lut)$_2$	70	248
$Cu(NCS)_2$(2,5-lut)$_2$	70	254
$Cu(NCS)_2$(2,6-lut)$_2$	70	248

For the complex compounds with L = 3- and 4-picoline, and 3,5- and 3,4-lutidine, the signal intensity from Cu(II) at the beginning of the measurement was greater than or nearly the same as that from Cu(I) obtained due to the decomposition of the compounds during storage (Fig. 1).

The X-ray electron spectra data showed the stability of the compounds $Cu(NCS)_2L_2$ with L = picoline or lutidine with a methyl substituent at position 2 to be distinctly lower in the surface layers.

Thermal properties of $Cu(NCS)_2(py)_2$

The TG and DTG curves for the thermal decomposition of this compound are shown in Fig. 3. Under the present experimental conditions up to 220° the heterocyclic base is released in one step. On increase of the temperature to 600°, the courses of the TG and DTG curves show that the intermediate obtained undergoes further thermal changes.

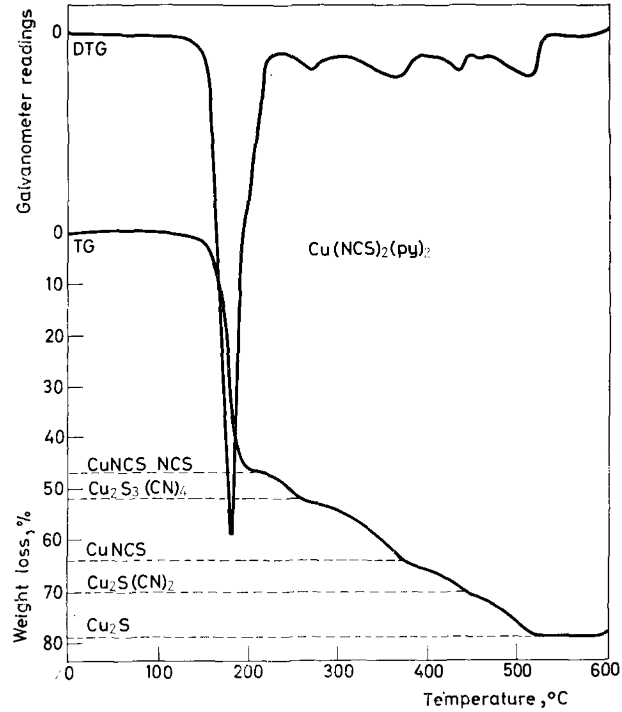

Fig. 3. Thermal curves of the compound $Cu(NCS)_2(py)_2$

The stoichiometry of thermal decomposition of $Cu(NCS)_2(py)_2$ may be expressed by the scheme:

$$Cu(NCS)_2(py)_2 \xrightarrow[I]{-2py} CuNCS \cdot NCS \xrightarrow[II]{-0.5\ S} CuS_{1.5}(CN)_2$$

$$\xrightarrow[III]{-0.5\ S-CN} CuNCS \xrightarrow[IV]{-0.5\ S} CuS_{0.5}\,CN \xrightarrow[V]{-CN} CuS_{0.5}$$

The calculated and the found weight losses for the different steps are listed in Table 2.

The suggested scheme for the thermal decomposition stoichiometry of $Cu(NCS)_2(py)_2$ may be supported by the following:

1. The existence and properties of the intermediates formed in steps I and II of thermal decomposition ($CuNCS \cdot NCS$ and $Cu_2S_3(CN)_4$) were discussed in detail in [5].

2. The suggested formation of CuNCS as the intermediate in step III is supported by the fact that in the diffractograms of the intermediates $CuNCS \cdot NCS$ and $Cu_2S_3(CN)_4$ all diffractions for CuNCS were identified by phase analysis [5].

Hunter et al. [8] characterized the compound CuNCS ·NCS as a substance with the lattice of copper(I) thiocyanate, containing polymeric thiocyanate groups. The properties of the compound $S(CN)_2$ released in step III of thermal decomposition are described by Fehér et al. [9] within a series of cyansulphanes of the general formula $S_{1-8}(CN)_2$.

Table 2

Values of the loss of weight in the different steps of thermal decomposition of $Cu(NCS)_2(py)_2$

Step of thermal decomposition	Loss of weight, %		Formula of the intermediate
	calc.	found	
I	46.82	47	CuNCS · NCS
II	51.56	52	$Cu_2S_3(CN)_4$
III	64.01	64	CuNCS
IV	68.75	70	$Cu_2S(CN)_2$
V	76.45	79	Cu_2S

3. The suggested stoichiometry of thermal decomposition of CuNCS in steps IV and V is in agreement with the data published by Bacanov and Zalivina on the thermal behaviour of CuNCS in a nitrogen atmosphere [10].

Thermal properties of $Cu(NCS)_2(3,5\text{-}lut)_2$

According to the thermal curves of all the investigated compounds with picolines and lutidines, only $Cu(NCS)_2(3,5\text{-lut})_2$ shows a similar behaviour to that of $Cu(NCS)_2(py)_2$ during its thermal decomposition. The TG and DTG curves of the thermal decomposition are shown in Fig. 4.

For this compound the DTG curve also shows a rather marked change of the decomposition rate as a function of temperature up to 280°. In the temperature interval 300–600° further decomposition steps were observed, in the same temperature intervals as for $Cu(NCS)_2(py)_2$. An analytical evaluation and the properties of the intermediate formed after step I of the thermal decomposition showed that this compound, of the composition $Cu_2S_3(CN)_4$, has the same properties as that formed by the thermal decomposition of $Cu(NCS)_2(py)_2$.

The stoichiometry of thermal decomposition of $Cu(NCS)_2(3,5\text{-lut})_2$ may be expressed by the scheme:

$$Cu(NCS)_2(3,5\text{-lut})_2 \xrightarrow[\text{I}]{-\,2(3,5\text{-lut})\ -0.5\ S} CuS_{1\cdot5}(CN)_2$$

$$\xrightarrow[\text{II}]{-0.5\ S-CN} CuNCS \xrightarrow[\text{III}]{-0.5\ S} CuS_{0\cdot5}CN \xrightarrow[\text{IV}]{-\,CN} CuS_{0\cdot5}$$

The calculated and the found weight losses in the different steps of the thermal decomposition are listed in Table 3.

In the thermal decomposition of $Cu(NCS)_2(3,5\text{-lut})_2$ the release of the sulphur atoms occurs in the first step, following the release of the heterocyclic base. The

Table 3

Values of the loss of weight in the different steps of thermal decomposition of $Cu(NCS)_2(3,5\text{-lut})_2$

Step of thermal decomposition	Loss of weight, %		Formula of the intermediate
	calc.	found	
I	58.46	61	$Cu_2S_3(CN)_4$
II	69.13	69	$CuNCS$
III	73.15	74	$Cu_2S(CN)_2$
IV	79.81	80	Cu_2S

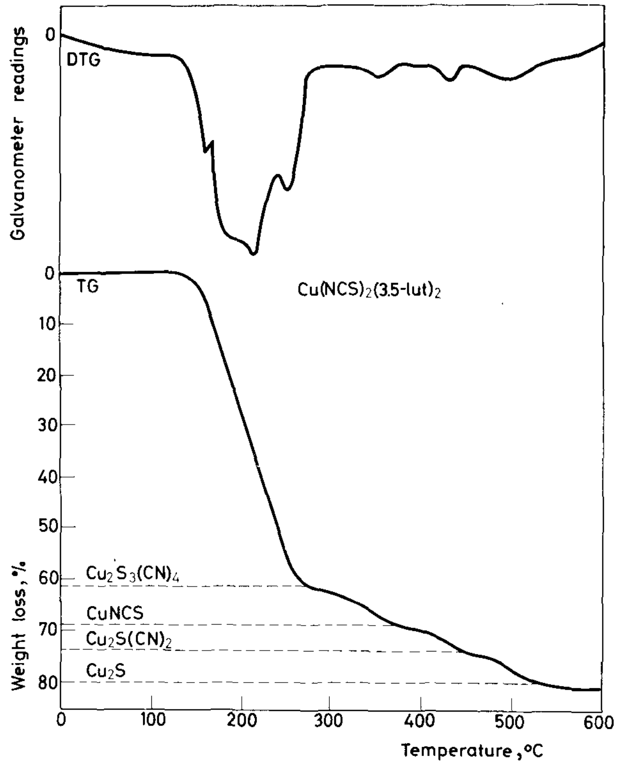

Fig. 4. Thermal curves of the compound $Cu(NCS)_2(3,5\text{-lut})_2$

same was observed for α-$Cu(NCS)_2(py)_2$ too, when the thermal decomposition proceeded in the air and the heating rate was slower [5].

Thermal properties of $Cu(NCS)_2L_2$

(L = 2-pic, 3-pic, 4-pic, 2,3-lut, 2,4-lut, 2,5-lut, 2,6-lut and 3,4-lut)

The curves for this group of compound differ significantly from those of the compounds discussed above. Up to ≈300° the DTG curves for these compounds show a rather complicated course, being different for the particular compounds. Figure 5 presents the curve of $Cu(NCS)_2(2,4\text{-lut})_2$ for illustration.

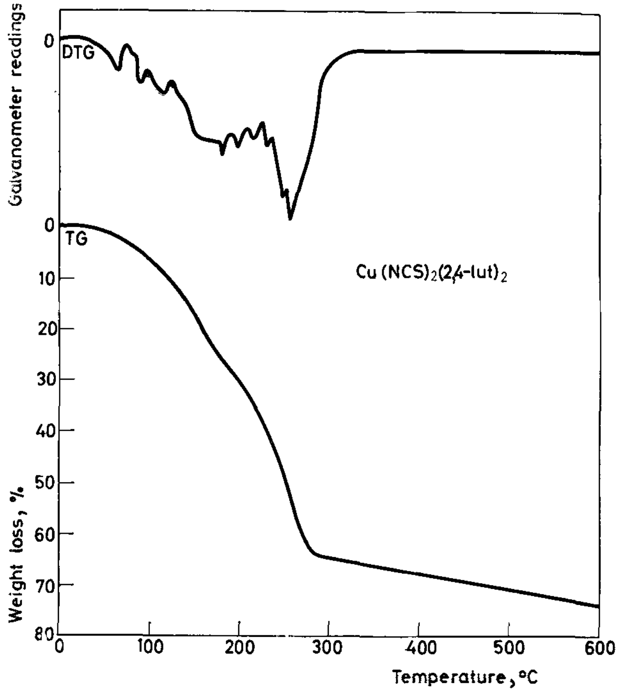

Fig. 5. Thermal curves of the compound $Cu(NCS)_2(2,4\text{-lut})_2$

For the compounds of this group the main decomposition takes place up to ≈300°. In the interval 300–600° the DTG curve does not register any changes, while the TG curve shows only a uniform loss of weight of the sample with temperature. The intermediates after the first decomposition step have nonstoichiometric composition and are of greater thermal stability than the thermal decomposition intermediates of the analogous compounds with pyridine and 3,5-lutidine.

General findings on the thermal decomposition of thiocyanatocopper(II) compounds with picolines and lutidines

It follows from the above that for the investigated thiocyanatocopper(II) coordination compounds with picolines and lutidines (except for $Cu(NCS)_2$ $(3,5\text{-lut})_2)$ the thermal stability of the coordinated NCS groups is significantly lower compared with that in $Cu(NCS)_2(py)_2$. The reactions connected with polymerization and the decomposition of the NCS groups were observed for $Cu(NCS)_2(py)_2$ in four separate steps (up to ≈280, ≈370, ≈440 and ≈520°). For the other coordination compounds the stoichiometries of thermal decomposition were not studied, since the methyl substituent on the pyridine ring markedly lowers the thermal stability of the coordinated NCS groups. The reactions connected with the polymerization and with the initial decomposition of the NCS groups are shifted into the temperature region up to 300° and coincide with the release of the ligand L.

References

1. M. KABEŠOVÁ, J. KOHOUT and J. GAŽO, Mh. Chemie, 107 (1976) 641.
2. J. KOHOUT, M. KABEŠOVÁ and J. GAŽO, Mh. Chemie 108 (1977) 1011.
3. J. GAŽO, I. B. BERSUKER, J. GARAJ, M. KABEŠOVÁ, J. KOHOUT, H. LANGFELDEROVÁ, M. MELNIK, M. SERÁTOR and F. VALACH, Coord. Chem. Rev., 19 (1976) 253.
4. J. GAŽO, M. KABEŠOVÁ, F. VALACH and M. MELNIK, Coord. Chim., 2 (1976) 715.
5. L. MACÁŠKOVÁ, M. KABEŠOVÁ, J. GARAJ and J. GAŽO, Mh. Chemie, 104 (1973) 1473.
6. F. PAULIK and L. ERDEY, Z. Anal. Chem., 160 (1958) 241.
7. L. ERDEY and G. LIPTAY, Periodica Polytech., 7 (1963) 223; CA 60 (1964) 8647.
8. J. A. HUNTER, W. H. S. MASSIC, J. MEIKLEJOHN and J. REID, Inorg. Nucl. Chem. Letters, 5 (1969) 1.
9. F. FEHÉR and H. WEBER, Chem. Ber., 91 (1958) 642.
10. C. C. BACANOV and E. N. ZALIVINA, J. Neorg. Chim., 17 (1972) 306.

RÉSUMÉ — L'article a trait aux propriétés thermiques des composés de coordination de composition $Cu(SCN)_2L_2$ (L = pyridine, 2-, 3-, 4-picoline, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-lutidine). La décomposition thermique de ces composés commence avec la libération du ligand L. Les composés avec des dérivés de la pyridine contenant un substituant méthyle en position 2 sur le cycle de la pyridine présentent une température initiale de décomposition qui se trouve abaissée de manière appréciable. On observe que le traitement aux rayons X provoque une réduction de l'atome central Cu(II) dans les composés de coordination étudiés. Les données fournies par les spectres électroniques des rayons X ont montré que la stabilité des composés $Cu(SCN)_2L_2$ avec L = picoline ou lutidine, ayant un substituant méthyle en position 2, est nettement plus faible dans les couches superficielles. Dans cette série de composés, $Cu(SCN)_2$ (pyridine)$_2$ et $Cu(SCN)_2$(3,5-lutidine)$_2$ montrent, en atmosphère d'azote, jusqu'à 600°, un processus analogue de décomposition thermique. La stoechiométrie de leur réaction de décomposition thermique est examinée.

ZUSAMMENFASSUNG — Der Artikel befaßt sich mit den thermischen Eigenschaften von Koordinationsverbindungen der Zusammensetzung $Cu(NCS)_2L_2$ (L = Pyridin, 2-, 3-, 4-Pikolin, 2,3-, 2.4-, 2,5-, 2,6-, 3,4- und 3,5-Lutidin). Die thermische Zersetzung dieser Verbindungen beginnt mit der Abspaltung des Liganden L. Die Verbindungen mit Pyridinderivaten, welche einen Methylsubstituenten in Position 2 im Pyridinring enthalten, zeigen eine deutlich herabgesetzte anfängliche Zersetzungstemperatur. Es wurde gefunden, daß die Röntgenbestrahlung eine Reduktion des zentralen Cu(II)-Atoms bei den untersuchten Koordinationsverbindungen herbeiführte. Die Daten der Röntgen-Elektronenspektren zeigten, daß die Stabilität der Verbindungen $Cu(NCS)_2L_2$ mit L = Pikolin oder Lutidin, welche einen Methylsubstituenten in Position 2 enthalten, in den Oberflächenschichten wesentlich geringer ist. Von der gegebenen Reihe der Verbindungen zeigen $Cu(NCS)_2$(Pyridin)$_2$ und $Cu(NCS)_2$(3,5-Lutidin)$_2$ in Stickstoff-Atmosphäre bis zu 600° einen ähnlichen Verlauf der thermischen Zersetzung. Die Stöchiometrie ihrer thermischen Zersetzung wird beschrieben.

Резюме — Изучены термические свойства координационных соединений состава $Cu(NCS)_2L_2$ где L = пиридгин, 2-, 3-, 4-пиколин, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-лутидин. Термическое разложение этих соединений начинается с выделения лиганда L. Соединения с 2-метилизамещенными пиридина показывают значительное уменьшение начальной температуры разложения. Обнаружено, что облучение рентгеновскими лучами при исследовании координационных соединений, вызывает восстановление центрального атома Cu(II). Данные рентгеновских электронных спектров показали, что стабильность соединений $Cu(NCS)_2L_2$ с L = пиколин или лутидин, имеющих метильную группу в положении 2, заметно ниже в поверхностных слоях. Из данной серии соединения $Cu(NCS)_2$ (пиридин)$_2$ и $Cu(NCS)_2$ (3,5-лутидин)$_2$ показывают аналогичный ход термического разложения в атмосфере азота до 600°. Обсуждена стехиометрия термического разложения этих соединений.