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

M. Kabešová, T. Šramko, J. Gažo, E. K. Zumadilov* and V. I. Nefedov*

Department of Inorganic Chemistry
Slovak Technical University, 880 37 Bratislava, Czechoslovakia
N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Science, Moscow, U.S.S.R.

(Received April 7, 1977)

The thermal properties of coordination compounds of the composition Cu(NCS)₂L₂ (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)₂L₂ 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-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)₂L₂, 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 compounds Cu(NCS)₂L₂ (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-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)₂L₂.
Experimental

Preparation of the compounds

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

Apparatus

The thermal decomposition of the compounds 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°C, with a heating rate of 9°C/min. The measurements were made in a nitrogen atmosphere.

The influence of X-ray radiation was studied by means of the Cu$^{2+}$p$_{3/2}$ line of these compounds on a VII–E–15 X-ray electron spectrometer. The spectra were excited by the Mg$K_α$ line at 10$^{-6}$ torr. Figure 1 shows the data of the Cu$^{2+}$p$_{3/2}$ line measured during radiation of Cu(NCS)$_2$(3,5-lut)$_2$. Figure 2 presents the

![Fig. 1. Change of the line Cu2p$_{3/2}$ in dependence on the radiation time](image)