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## Abstract

## Full Text

A. L. DOROSINSKII, O. V. KOLNINOV, Z. V. ZVONKOVA, G. S. ZHDANOV

# X-RAY AND SPECTRAL STUDY OF COMPLEX COMPOUNDS OF THIOCYANATE OF MONOVALENT COPPER WITH THIOUREA AND PYRIDINE

*(Presented by Academician S. S. Medvedev on February 19, 1963)*

It has been established <sup>(1)</sup> that the thiocyanate group can attach to a metal atom M in three different ways, with formation of the following chemical bonds: M—SCN, M—NCS, —M—SCN—M—. This discovery aroused considerable interest. A systematic comparison of X-ray structural and spectral data, carried out in a number of studies, led to the possibility of rapidly determining the mode of coordination of the SCN group in various complex compounds from the frequencies of their infrared spectra <sup>(2-4)</sup>.

In the present work, by the X-ray method, the chemical formulas of two new complex compounds of cuprous thiocyanate with thiourea and with pyridine have been established.

By means of infrared spectroscopy, the different character of the bond of the thiocyanate group in copper thiocyanate and in its complex with thiourea has been found.

An attempt to obtain a complex compound of cuprous thiocyanate with thiourea was undertaken as early as 1903 <sup>(5)</sup>. However, the authors erroneously note that when copper thiocyanate is dissolved in an aqueous solution of thiourea, no complex compound is formed owing to the low solubility of CuSCN. Later, the product of the interaction of  $[\text{Cu}(\text{CSN}_2\text{H}_4)_3]\text{Cl}$  and  $\text{NH}_4\text{CNS}$  in aqueous solution was studied <sup>(6)</sup>. In this case an oily substance was formed. Its composition lay between  $[\text{Cu}(\text{CSN}_2\text{H}_4)_3]\text{SCN}$  and  $[\text{Cu}(\text{CSN}_2\text{H}_4)_2 \cdot \text{H}_2\text{O}]\text{SCN}$ . It was not possible to determine unambiguously the chemical formula of the compound.

In the present work, copper thiocyanate was dissolved in an aqueous solution of thiourea. On standing, an oily substance separated from the solution; from it large colorless single crystals were obtained. After the crystals had been melted (m.p. 88—89°), the melt in the supercooled state again forms a viscous mass, which subsequently gradually solidifies. This substance has plastic properties; it is capable of being molded and drawn out into long threads. The chemical formula of this compound was established on the basis of X-ray structural data, in the same way as had been done earlier in <sup>(7)</sup>. The parameters of the elementary cell are:  $a = 11.9$ ,  $b = 8.7$ ,  $c = 17.4$  Å,  $\beta = 130^\circ$ . The Fedorov group is  $P2_1/C$ .

The pycnometric density, determined by A. N. Abramova,  $\sigma = 1.66 \text{ g/cm}^3$ . Proceeding from the general fourfold position  $4(e)$  of the group  $P2_1/C$ , the number of molecules in the cell  $z$  was taken equal to four. Hence the molecular weight of the compound under investigation was calculated:

$$\text{Mol. wt. (X-ray)} = \frac{v\sigma}{1.65 \cdot z} = \frac{1380 \cdot 1.66}{1.65 \cdot 4} = 347.$$

Salts of monovalent copper form with thiourea complexes of composition  $\text{CuX} \cdot 2\text{CSN}_2\text{H}_4$  and  $\text{CuX} \cdot 3\text{CSN}_2\text{H}_4$  <sup>(8)</sup>. In work <sup>(9)</sup> the crystal structure of  $\text{ClCu} \cdot 3\text{CSN}_2\text{H}_4$  was determined. The complex compound of composition  $\text{CuSCN} : \text{CSN}_2\text{H}_4 = 1 : 2$  has mol. wt. 274, whereas for the complex of composition  $\text{CuSCN} : \text{CSN}_2\text{H}_4 = 1 : 3$  it is equal to 350, which agrees fairly well with the value calculated from the structural-analysis data. Consequently, for the substance under study the composition  $\text{NCSCu} \cdot 3\text{SC}(\text{NH}_2)_2$  may be accepted, which is confirmed by chemical-analysis data.

Found %:	Cu 18.10;	S 36.00*;	C 14.23;	N 28.28	H 3.38
$\text{NCSCu} \cdot 3\text{SC}(\text{NH}_2)_2$ . Calculated %:	Cu 18.15;	S 36.70;	C 13.75;	N 28.00	H 3.42

\* The sulfur content was calculated by difference from 100%.

We obtained the IR spectra of  $\text{CuSCN}$  and  $\text{NCSCu} \cdot 3\text{SC}(\text{NH}_2)_2$ . It is known from the literature that, in the case of a strong bridging bond  $-\text{M}-\text{SCN}-\text{M}-$ , the frequency of the stretching vibrations of the C N group in the IR spectra increases and has a value of about  $2150 \text{ cm}^{-1}$  <sup>(2)</sup>. The appearance of a band belonging to the C=S group in the region  $694-738 \text{ cm}^{-1}$  indicates coordination  $\text{M}-\text{SCN}$ , and in the region  $760-880 \text{ cm}^{-1}$  coordination  $\text{M}-\text{NCS}$  <sup>(3)</sup>. In the spectrum of  $\text{CuSCN}$ , the frequency of the stretching vibration of the C N group was found at  $2160 \text{ cm}^{-1}$ , which agrees well with the literature data <sup>(10)</sup>. Consequently, copper thiocyanate has a polymeric chain structure  $-\text{Cu}-\text{SCN}-\text{Cu}-$ , as does silver thiocyanate, whose crystal structure was previously deciphered <sup>(11)</sup>. In the spectrum of  $\text{NCSCu} \cdot 3\text{SC}(\text{NH}_2)_2$  this frequency is  $2060 \text{ cm}^{-1}$ . It follows from this that, in the formation of the complex compound of copper thiocyanate with thiourea, the polymeric chain is broken. The observed frequency of  $745 \text{ cm}^{-1}$  does not make it possible to establish unambiguously the presence of a Cu-S or Cu-N bond.

The complex compound of cuprous thiocyanate with pyridine was obtained by dissolving  $\text{CuSCN}$  in anhydrous pyridine. The crystals are fairly stable in solution, but in air they rapidly become cloudy. Therefore, for X-ray photographs the crystals were covered with a layer of paraffin.

The chemical formula of this compound was also established on the basis of X-ray data. The unit-cell parameters are:

$a = 5.8$ ,  $b = 14.2$ ,  $c = 14.8 \text{ \AA}$ ,  $\beta = 100^\circ$ . Space group  $C_{2h}^5 - P2_1/C$ . Pycnometric density  $\sigma = 1.53 \text{ g/cm}^3$ .

Taking  $z = 4$ , we find from the X-ray data the molecular weight of the compound under study:

$$\frac{1208 \cdot 1.53}{1.65 \cdot 4} = 280.$$

This value leads to the chemical formula  $\text{NCSCu} \cdot 2\text{N}$  (mol. wt. 280).

On the basis of the foregoing it was concluded that, in contrast to  $\text{NCSCu} \cdot 3\text{SC}(\text{NH}_2)_2$ , this substance is a complex compound containing two formula units of pyridine per one formula unit of copper thiocyanate. The results of chemical analysis are as follows:

$\text{NCSCu} \cdot 2\text{N}$ . Found %: Cu 24.58; S 12.68; C 46.59; N 12.66 H 3.67  
 Calculated %: Cu 22.80; S 11.48; C 47.30 N 15.05 H 3.61

Some discrepancy between the calculated values and the chemical-analysis data should be attributed to decomposition of the complex during the analysis. Further calculations of three-dimensional syntheses of the electron density of the crystals will make it possible to refine the crystal structures and to provide additional information on the nature of the chemical bond in complex compounds of cuprous thiocyanates.

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 named after L. Ya. Karpov

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