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The Crystal Structure of Copper(I) Thiocyanate and its Relation to the Crystal Structure of Copper(II) Diammine Dithiocyanate Complex

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Well developed crystals of copper(I) thiocyanate, CuNCS, are formed by decomposition of $Cu(NH_3)_2(NCS)_2$ in aqueous solution. They belong to the orthorhombic system, the space group is Pbca, a = 10.994(9) Å; b = 7.224(3) Å; c = 6.662(2) Å, and there are eight formula units in a unit cell. The structure was refined by the method of full matrix least squares, yielding the value 0.062 for the R factor. All thiocyanate groups are approximately linear in the crystal structure and they are fourdentate, bonding in the form of bridges. Each copper atom is tetrahedrally coordinated by three sulphur atoms (the distances Cu–S being in the interval 2.34–2.37 Å) and by the nitrogen atom (Cu–N = 1.93 Å). Each sulphur atom is tetrahedrally coordinated by three copper atoms and one carbon atom (S–C = 1.70 Å). The relation between the crystal structures of $Cu(NH_3)_2(NCS)_2$ and CuNCS are discussed.

Introduction

Copper(II) salts in the presence of the thiocyanate group may be easily reduced. The resulting products are copper(I) thiocyanate, CuNCS, and $(NCS)_2$, but they may undergo further chemical changes[1,2]. The existence of modifications of CuNCS has been already reported several times[3–5].

Formation of these modifications depends on the preparation procedure. Thus *e.g.*, the white form conventionally designated as α-CuNCS precipitates from the system $CuSO_4$–NH_4NCS–H_2O. The brown CuNCS, called the β-modification, is formed when carbonates are present in the above system[5]. The present report gives results concerning the crystal structure of white CuNCS and the mutual relation between the crystal structure of $Cu(NH_3)_2(NCS)_2$ and that of the white CuNCS.

Experimental

Preparation

Modifications of CuNCS were prepared by slow reduction of the crystals of $Cu(NH_3)_2(NCS)_2$ in the parent solution at 50° C. Crystals of $Cu(NH_3)_2(NCS)_2$ were crystallized from the system $CuSO_4$–NH_3–NH_4NCS–H_2O, at room temperature[6]. After two or three weeks the brown β-modification of CuNCS was formed from crystals of $Cu(NH_3)_2(NCS)_2$ in solution. In the case in which the process was not interrupted, it was transformed to the white α-CuNCS. The white and brown modifications of CuNCS were in this way prepared in single crystal form. *Analysis:* (M = 121.62) Calcd. Cu 52.24%, S 26.36%; Found: Cu 52.20%, S 26.33% (white CuNCS); Cu 52.21%, S 26.30% (brown CuNCS). The copper content was determined complexometrically[7]. The sulphur content was found in the form of $BaSO_4$ after alkaline oxidative remelting of the samples.

Collection of X-ray Data

The unit cell dimensions and intensity data were measured on Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite crystal monochromator, using MoK_α radiation. A least-squares fit of the four position angles for fifteen reflections produced the orientation matrix required to control data collection and afforded the following unit cell dimensions: $a = 10.994(9)$ Å; $b = 7.224(3)$ Å; $c = 6.662(2)$ Å; V = 529.1(5) $Å^3$. Assuming a value of Z equal to 8, the density 3.05 g cm^{-3} was calculated, $D_{Meas.}$ = 2.98 g cm^{-3}. The crystal belongs to the orthorhombic system with the space group Pbca (No. 61)[8].

Data were collected in the range of $0° < 2\Theta \leqq 100°$. The Θ– 2Θ scan technique with a variable scan rate from 4.0 to 24.0 deg min^{-1} was used. The scan range was from $2\Theta(MoK_{\alpha_1})-1°$ to $2\Theta(MoK_{\alpha_2}) + 1°$. The background counts were taken at each end of the

TABLE I. Fractional Atomic Coordinates (x 10^5) and Anisotropic Temperature Factors (x 10^2) for the Independent Part of the Atoms of CuNCS.[a]

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	18428(8)	15640(13)	13598(15)	111(3)	197(4)	229(4)	16(3)	0(3)	–6(3)
S	78357(15)	38390(23)	17407(26)	102(6)	106(6)	121(6)	14(4)	10(4)	–7(5)
N	1656(50)	23210(97)	11760(101)	101(21)	290(29)	205(27)	33(21)	7(21)	–13(24)
C	92453(61)	29429(93)	13919(113)	142(26)	154(28)	136(26)	8(19)	–16(21)	–1(24)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

range for a time equal to one half of the scan time. The intensity I was equal to scan rate [total scan counts–(sum of background counts)/background to scan ratio] with a $\sigma(I)$ equal to the scan rate [total scan counts + (sum of background count/background to scan ratio)$^2]^{1/2}$. In order to check the stability of the measurement two reflections were selected as standards and their intensities were recorded periodically through data collection (every 320 reflections). Their intensities showed no significant change with time. The 1496 reflections were collected including systematic absences. The 856 reflections with $I > 1.96(I)$ were used in the analysis. The intensities and their standard deviations were corrected for Lorentz polarization factor, the polarization of the monochromator and simple absorption correction. (The linear absorption coefficient was 89.4 cm^{-1} for MoK_α).

Refinement of X-ray Data

The copper atom was immediately located in a three–dimensional Patterson map. The solution and the refinement of the structure was carried out by the usual sequence of Fourier syntheses and full-matrix least-squares refinements. The positions and temperature factors of all atoms were in the first step refined isotropically using a block-diagonal matrix. The function minimized was: $\Sigma w(|F_o|-|F_c|)^2$ and $w = \frac{1}{\sigma_F^2}$, where $\sigma_F = (F_o^2 + \sigma_I/L_p)^{1/2}-F_o$. After three cycles the discrepancy indices of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.109$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.093$ were reached at convergence. At this stage two cycles of full-matrix anisotropic refinement was applied (a total of 37 varied parameters). The final R value was R = 0.062. Parameter changes in the final cycle were all less than 0.25 times the esd of the parameter. The refined atomic positions and anisotropic temperature coefficients are listed in Table I. The observed and calculated structure factors of white CuNCS are available on request from the Editor.

All calculations were carried out on an CDC-3300 computer using the programs written by P. Gantzel, R. Sparks and K. Trueblood; DRF and DISTAN by A. Zalkin. All mentioned programs were modified by O. Lindgreen. The atomic scattering factors were from Cromer and Wabers[9] for all atoms.

Description of the Crystal Structure

The crystal structure of the white modification of CuNCS forms a three-dimensional skeleton, consisting of mutually interlinked, nearly linear formations of CuNCS. The coordination polyhedrons around the copper(I) atoms have the shape of distorted tetrahedrons. The apexes of the tetrahedrons are occupied by three sulphur and one nitrogen atoms. The interatomic distances Cu–S are in the range 2.34–2.37 Å (see Fig. 1 and Table II). The bond length Cu–N has the value 1.93 Å. The distorted tetrahedrons around the copper(I) atoms are mutually linked by their apexes which are occupied by sulphur atoms. Each sulphur atom is shared by three tetrahedrons. Tetrahedrons linked in this way form layers that are perpendicular to the *x* axis. These layers are interlinked by the groups NCS. *E.g.*, the nitrogen atom from the thiocyanate group belongs to the apex of a tetrahedron of the one layer and the sulphur atom of the same thiocyanate group belongs to the apex of the tetrahedron of the neighbour layer (see Fig. 1). The thiocyanate groups are, within the limits of experimental precision, linear. The most important interatomic distances and

TABLE II. Some Interatomic Distances and Bond Angles for CuNCS.[a]

Atoms	Interatomic Distances [Å]	Atoms	Bond Angles [°]
		S(1)–Cu–S(3)	103.01(7)
Cu–S(1)	2.354(2)	S(1)–Cu–S(2)	107.28(7)
Cu–S(2)	2.367(2)	S(2)–Cu–S(3)	110.15(7)
Cu–S(3)	2.344(2)	S(1)–Cu–N	115.02(20)
Cu–N	1.927(6)	S(2)–Cu–N	114.39(20)
N–C	1.116(9)	S(3)–Cu–N	106.31(20)
C–S	1.696(7)	S–C–N	178.66(68)

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

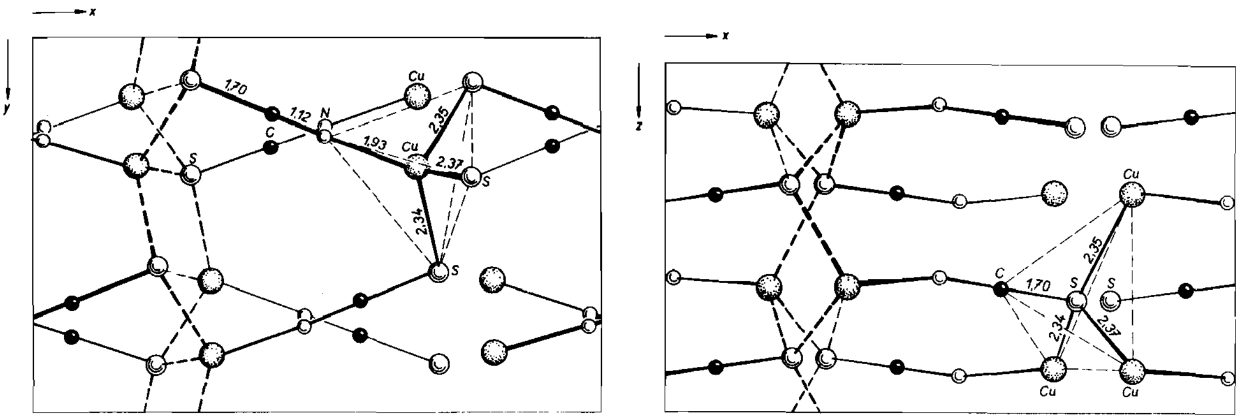

Figure 1. The crystal structure of CuNCS in the (001) and (010) projections.

bond angles of CuNCS are shown in Table II. The found interatomic distances in the studied thiocyanate group do not diverge from the range of values found for other thiocyanate Cu(II) compounds (see Table III.)

In preparing the CuNCS crystals an interesting observation was made. In the process of decomposition, the crystals of $Cu(NH_3)_2(NCS)_2$ are transformed to the crystals of CuNCS in such a way that no observable changes in number, habitus and orientation of the

TABLE III. Interatomic N–C and S–C Distances and Bond Angles of NCS Groups in Some Cu(II) Coordination Compounds

Compounds	Type of Bonding of NCS Groups	Angles in NCS Groups [°]	Distances [Å]		Ref.
			C–N	C–S	
$Cu(NH_3)_2(NCS)_2$	α Cu(II)–NCS	176	1.145	1.635	[10]
	α Cu(II)–NCS$\begin{smallmatrix}\nearrow \mathrm{Cu(II)}\\ \searrow \mathrm{Cu(II)}\end{smallmatrix}$	178	1.164	1.609	
	β Cu(II)–NCS	160	1.372	1.670	
	β Cu(II)–NCS$\begin{smallmatrix}\nearrow \mathrm{Cu(II)}\\ \searrow \mathrm{Cu(II)}\end{smallmatrix}$	159	1.204	1.632	
$Cu(NH_3)_4(SCN)_2$	Cu(II)–SCN	–	1.170	1.630	[12]
$Cuen(NCS)_2$	Cu(II)–NCS	161.2	1.290	1.690	[13]
		154.7	1.320	1.650	
	Cu(II)–NCS$\begin{smallmatrix}\nearrow \mathrm{Cu(II)}\\ \searrow \mathrm{Cu(II)}\end{smallmatrix}$	172.3	1.250	1.680	
		165.0	1.240	1.710	
$Cu(en)_2(SCN)_2$	Cu(II)–SCN	176.9	1.160	1.620	[14]
$Cu_2(NH_3)_3(NCS)_3$	Cu(II)–NCS–Cu(II)	179.3	1.181	1.638	[15]
	Cu(I)–NCS–Cu(I)	176.3	1.127	1.671	
	Cu(I)–NCS$\begin{smallmatrix}\nearrow \mathrm{Cu(II)}\\ \searrow \mathrm{Cu(I)}\end{smallmatrix}$	175.1	1.128	1.710	

original crystals could be detected. Transformation of a copper(II) complex to a copper(I) complex is connected with changes in colour. Since the crystal structure of the starting crystal[10] and that of the final crystal were known, we attempted to show a scheme for the transformation of the crystal structure of $Cu(NH_3)_2(NCS)_2$ to that of CuNCS. These schemes are shown in Figures 2 to 5. The schematic drawing of the structure of $Cu(NH_3)_2(NCS)_2$ is shown in Figure 2.

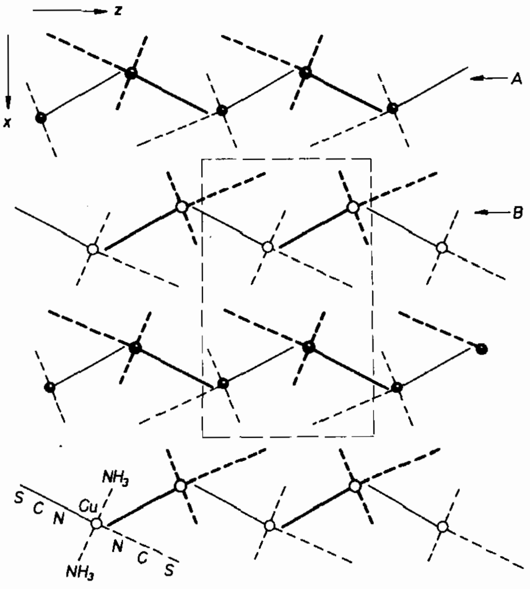

Figure 2. Schematic drawing of the crystal structure of $Cu(NH_3)_2(NCS)_2$ in the (010) projection.

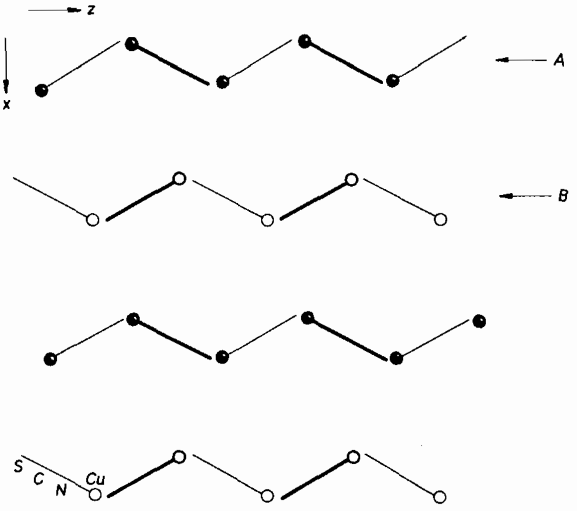

Figure 3. The first step of transformation of the crystal structure of $Cu(NH_3)_2(NCS)_2$ to that of CuNCS.

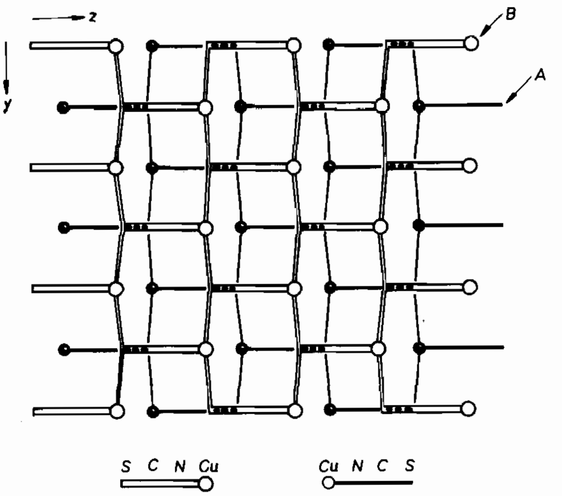

Figure 4. The hypothetical skeleton of Figure 3 in the (100) projection.

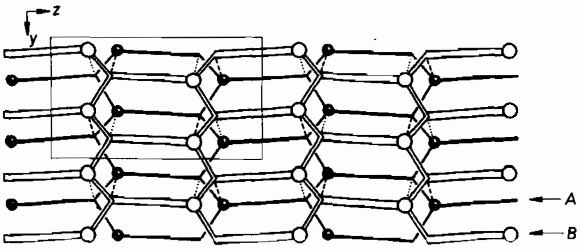

Figure 5. The second step of transformation of the crystal structure of $Cu(NH_3)_2(NCS)_2$ to that of CuNCS.

The dashed lines designate the mono-functionally coordinated thiocyanate groups and ammonia molecules. These are released in the course of the reduction process[11]. Different types of lines indicate the positions (1/4 and 3/4b) of the units $Cu(NH_3)_2(NCS)_2$ in the (010) projection. In this projection the sulphur atoms would fall within the area of copper atoms and therefore Cu–S bonds are not shown. A hypothetical skeleton which is formed after the ammonia molecules and the thiocyanate groups have been removed is shown in Figure 3. There are two layers (marked as A and B in Figure 3) with a different mutual orientation of the CuNCS groups. They occur already in the starting structure. All thiocyanate groups of the layer A are pointed to the right in relation to the copper atom, while they are oriented to the left in the layer B. The layers A and B of the hypothetical skeleton (Figure 4) are drawn by double and single lines. As shown in Figure 4 each layer consists of distorted hexagons. The original bonds of the copper atom, $\mathrm{N{-}Cu}{<}^{\mathrm{S}}_{\mathrm{S}}$, from the pseudooctahedral coordination are shown markedly. Since the copper and sulphur atoms in the crystal structure of CuNCS are coordinated pseudotetrahedrally, the changed bond angles around the copper and sulphur atoms are given in Figure 5. There are also shown all bonds between layers in Figure 5, including new bonds (marked by dashed lines) and the position of the unit cell, which corresponds in relation to its position to the unit cell in Figure 1. Comparison of Figure 1 and Figure 5 shows the agreement between the constructed structural scheme and the actual structure of CuNCS in the (010) projection.

From the above it follows that the transformation of the crystal structure of $Cu(NH_3)_2(NCS)_2$ to that of CuNCS may take place without significant reorganization of atoms or groups of atoms in the initial crystal structure. Those groups of CuNCS which occur in the initial and the resulting crystal structure keep their space orientation and all their original bonds. Any changes that will take place concern only the interatomic distances Cu–S, the angles around the copper and sulphur atoms.

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