

## THE NATURE OF THE STRUCTURAL DIFFERENCES BETWEEN THE MODIFICATIONS OF THE DITHIOCYANATE-DIAMINE CUPRIC COMPLEX

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Received January 19th, 1971

Using single crystal structure analysis, the structural differences between the modifications of  $\text{Cu}(\text{SCN})_2(\text{NH}_3)_2$  were localized. They are connected with the different degree of deviation from linearity of the thiocyanate groups, which are bonded by single bonds or by bridges. The modifications show in the crystal structure the same type of the central atom co-ordination and the same arrangement of the molecules of dithiocyanate-diamine cupric complex. Certain differences in some interatomic distances in the co-ordination polyhedron were also observed.

In a previous paper<sup>1</sup>, it was stated that the dithiocyanate-diamine cupric complex exists in various modifications. The modifications were identified using powder diffraction patterns on the basis of different diffraction intensities for the same diffraction angles. Besides the two limiting states, the existence of a number of structural intermediates was proved and they were called, analogously to the modifications of the dibromo-diamine cupric complex, transition compounds<sup>2</sup>. In the case of the modifications of the dibromo-diamine cupric complex (which have also been identified using diffraction patterns), the existence of a number of structural intermediates was observed for the first time<sup>3</sup>. The X-ray structure analysis of the two limiting states showed that the  $\text{CuBr}_2(\text{NH}_3)_2$  modifications differ in the degree of distortion of the co-ordination polyhedron around the central atom<sup>4,5</sup>. The experimentally proved states of distortion of the co-ordination polyhedra are, however, considered by some authors as the experimental proof of a predicted new type of isomerism due to the Jahn-Teller effect<sup>6,7</sup>. However, dibromo-diamine cupric complexes have not been prepared as single crystals and thus modifications of the dithiocyanate-diamine cupric complex were used for further investigations. These modifications are analogous to those of the dibromo-diamine cupric complex as to existence of transition compounds and also in other physico-chemical properties, *e.g.* in structural changes of the modifications observed under the effect of heat, time, and pressure. One of the two limiting states and several transition compounds of the dithiocyanate-diamine cupric complex have been successfully prepared in a chemically pure state and as single crystals<sup>8-10</sup>.

In the present paper single crystal X-ray analysis was applied to the study of the different modifications of the dithiocyanate-diamine cupric complex with different diffraction patterns.

## EXPERIMENTAL

*Preparation:* Single crystals of two modifications of the dithiocyanate-diamine cupric complex with substantially differing diffraction patterns were prepared for analysis according to the literature<sup>8</sup>. A sample of the  $\alpha$ -modification was prepared by slow crystallization from aqueous solution with high ratio  $[\text{NH}_3] : [\text{Cu(II)}] = 25$ , at room temperature. A sample of the  $\beta$ -modification was prepared by prolonged crystallization from aqueous solutions with the low ratio of  $[\text{NH}_3] : [\text{Cu(II)}] = 10$ , at the temperature of 40°C. The crystals were blue needles and for X-ray analysis they were covered with a film of lacquer. Analysis: For  $\text{Cu}(\text{SCN})_2(\text{NH}_3)_2$  (213.8) calculated: 29.76% Cu, 15.89%  $\text{NH}_3$ , 54.35% SCN; found: 29.82% Cu, 15.76%  $\text{NH}_3$ , 53.99% SCN; 29.73% Cu, 15.80%  $\text{NH}_3$ , 53.95% SCN.

*X-ray analysis:* The crystals of both modifications were analyzed using  $\text{CuK}_\alpha$  radiation. By the equi-inclination Weissenberg method, the layers h01—h41, 0k1, and hk0 were obtained. It follows from the literature<sup>8-10</sup> that the modifications of the dithiocyanate-diamine cupric complex, and especially its so-called "limiting states" (the thermodynamically unstable states), may easily undergo structure changes under the influence of various physicochemical conditions. It was also found that these substances are changed even by the effect of X-rays. The relatively long exposure time needed for obtaining Weissenberg pictures by film technique entails the danger that, during the time necessary for obtaining the number of pictures needed, structural changes may take place in the modifications and the studied differences between the modifications would not be detectable. For this reason, each layer was exposed using a new crystal, which was approximately of the same size and was taken from the same preparation solution. The suitability of the chosen crystal as far as identity was concerned was verified by comparing with the so-called reference zero layer: after obtaining the pattern of a particular layer, the pattern of the zero layer was taken using the same crystal. The patterns of the zero layers served for comparison of the geometry and the intensities of blackening of the diffractions obtained from different crystals. The crystal size varied within the range 0.3—0.6  $\times$  0.2 to 0.25  $\times$  0.15—0.2 mm.

*The unit cell and the space group:* Both kinds of analyzed crystals had orthorhombic symmetry. The diffraction angles of all traces in the Weissenbergograms of both the analyzed modifications were identical and the patterns differed only in the intensity of blackening of certain diffractions. The lattice constants were determined from the zero layers of the Weissenberg patterns, using calibration with NaCl as standard. Their values are:  $a = 13.94 \pm 0.02$ ,  $b = 6.01 \pm 0.01$ ,  $c = 8.81 \pm 0.01$  Å. The specific weight was determined by the immersion method using an acetone and bromoform solution: the calculated value is  $1.912 \text{ g cm}^{-3}$ ; the values found are 1.914 and  $1.912 \text{ g cm}^{-3}$ . The unit cell contains four formula units. According to the rules for quenching the reflections present, two space groups were determined:  $Pnma$  (No 62) and  $Pn2_1a Pna2_1$  (No 33) (ref.<sup>12</sup>).

*Determination of the crystal structure:* The blackening of the reflections was measured with the Zeiss non-registering microphotometer. The values measured were corrected for nonlinearity of the logarithm of the blackening dependence on the exposure time, were brought to a uniform scale, and corrected for the Lorentz polarization factor. No absorption correction was applied (the product  $\mu R = 1.195$ — $1.990$ ). The solution of the crystal structure was based on the three-dimensional Patterson function. The positions of the copper atoms were determined for both the modifications. These positions were identical, not only with each other, but also with the values of the co-ordinates for the copper atom positions in the solved crystal structure of the dithiocyanate-diamine cupric complex<sup>11-13</sup>. The Patterson functions for the modifications differed only in shifts or a changes of the shape of several maxima of the interatomic vectors. In Fig. 1 a section through the Patterson function  $w = 0$  for both modifications is compared with the so-

called theoretical Patterson function, which was calculated from the structural factors  $F_c$  in the paper<sup>11</sup>. The theoretical Patterson function gave information about the positions and shapes of all interatomic vectors for the atoms of the dithiocyanate-diamine copper(II), in which all atoms are located in the mirror plane of the space group  $Pnma$ . It followed from the comparison that the Patterson function of the  $\alpha$ -modification is very close to the arrangement and shape of interatomic vectors of the theoretical Patterson function, while the Patterson function of the  $\beta$ -modification showed small but evident differences. The deviation of the maximum  $F$  from the

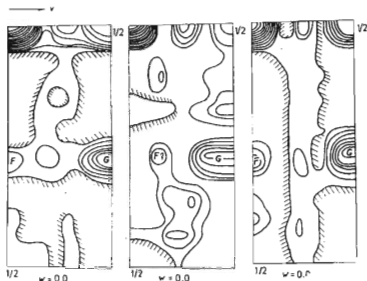


FIG. 1

Comparison of the Patterson Functions for  $\alpha$ - and  $\beta$ -Modifications of the Dithiocyanate-diamine Cupric Complex with the Theoretical Patterson Function for the Cut  $w = 0$

$a$   $\alpha$ -Cu(SCN)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>,  $b$   $\beta$ -Cu(SCN)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>,  $c$  Fc-Patterson function.

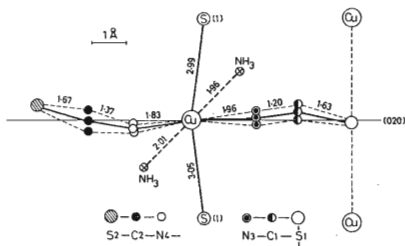


FIG. 2

Schematic Representation of the Molecule of the  $\beta$ -Modification of the Dithiocyanate-diamine Cupric Complex

The magnitudes of the standard deviations for the atoms of the thiocyanate groups in the  $y$ -co-ordinates are given by the dashed line.

plane  $\nu = 0$ , and the elongated shape of the maximum  $G$  in the case of the  $\beta$ -modification is in agreement with the assumptions following from the interpretation of the powder diffraction patterns in the paper<sup>10</sup>. It is assumed that the structure differences between the modifications are due to deviations of some atoms from the mirror plane of the space group  $Pnma$ . From the Fourier synthesis (calculated according to the centrosymmetrical space group  $Pnma$ ), it was found that also the co-ordinates of all other atoms were very close to those of the solved crystal structure<sup>11,13</sup>. The solution of the crystal structures of the modifications was, therefore, carried out according to the noncentrosymmetrical space group  $Pn2_1a$ . The scale constants, the general isotropic thermal factor, the atom co-ordinates, and the individual isotropic thermal factors were refined by the least squares method. After the refinement of all parameters, an  $R$ -factor of 0.15 was obtained for the  $\alpha$ -modification. No further maxima were identified by differential Fourier synthesis. The solution of the crystal structure of the  $\beta$ -modification was interrupted at the  $R$ -factor value, 0.25. From the interpretation of the other maxima of the differential Fourier synthesis (where the maximum electron density value was  $4e/\text{\AA}^3$ ) it followed that it might be a case of a different orientation of the molecules of the dithiocyanate-diamine cupric complex in its crystal structure, *e.g.* due to defects in the crystal lattice or to twinning of the crystals. Paper<sup>13</sup> also points to this fact. Crystal structure defects cannot be excluded either, since this limiting state was prepared for analysis by prolonged crystallization at a higher temperature. Orientative calculations showed that the potential possibilities for further decreasing the  $R$ -factor of this crystal are based on the interpretation of other maxima of the differential Fourier synthesis. The positions of the already determined atoms did not change very much and varied within the standard deviation; this fact follows also from the comparison of Figs 2 and 3a. In Fig. 2 the shape of the  $\beta$ -modification molecule is given in one of the preliminary stages of the solution of this crystal structure. The dashed lines in Fig. 2 show the magnitude of the standard deviations for the thiocyanate group atoms in the  $y$ -co-ordinates.

*Calculation of the crystal structures:* The correction for the Lorentz polarization factor was carried out with the ZPA-1 computer in the Slovak Academy of Sciences, Computing Centre Bratislava, according to<sup>14</sup>. The Patterson and Fourier syntheses were carried out in the Computing Centre at the Göteborg University, using the IBM 360/50 computer, according to<sup>15</sup>.

The least-square refinement was carried out with the IBM 7040 computer in the Computing Centre of the Ministry of Planning, Bratislava, according to the literature<sup>16</sup>, and with the IBM 360/50 computer in the Computing Centre at the Göteborg University, according to the literature<sup>17</sup>. The calculation of angles and interatomic distances was carried out with the Gier computer in the Computing Centre, Slovak Academy of Sciences, Bratislava, according to the literature<sup>18</sup>.

## RESULTS AND DISCUSSION

The results of the single crystal X-ray structure analysis showed that both modifications (and probably also the transition substances) keep the same system of arrangement of the molecules in the crystal structure. The Cu(II) central atom has, in both cases, the co-ordination number of six. It is co-ordinated in a plane by two nitrogen atoms from the ammonia molecules, and the two remaining *trans*-positions, are occupied by two thiocyanate groups bonded through nitrogen. In the vertical positions, the co-ordination is completed by two Cu—S van der Waals bonds. The co-ordination polyhedron has, in both cases, the shape of an elongated bi-pyramid.

In Figs 3a and 3b the shapes of the molecules are schematically given determined

TABLE I  
Interatomic Distances (Å) (and their E.S.D.) in the  $\alpha$ - and the  $\beta$ -Modifications of the Dithiocyanate-diamine Cupric Complex

Complex	$\alpha$ -Modification	$\beta$ -Modification
Cu—S(1)	3.11 (4)	3.05 (6)
Cu—S(1)	2.93 (4)	2.99 (6)
Cu—N(3)	1.96 (3)	1.96 (7)
Cu—N(4)	1.91 (3)	1.83 (7)
N(3)—C(1)	1.20 (4)	1.20 (9)
N(4)—C(2)	1.21 (4)	1.37 (9)
C(1)—S(1)	1.62 (3)	1.63 (9)
C(2)—S(2)	1.64 (3)	1.67 (7)
Cu—NH <sub>3</sub>	2.02 (3)	2.01 (9)
Cu—NH <sub>3</sub>	1.20 (2)	1.95 (7)

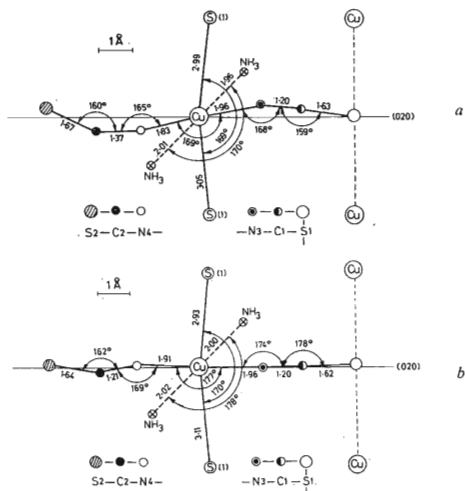


FIG. 3

Schematic Representation of the Molecular Shapes of the  $\alpha$ -*a* and  $\beta$ -*b* Modifications of the Dithiocyanate-diamine Cupric Complex

TABLE II

The Practical Co-ordinates of Atoms of the  $\alpha$ - and the  $\beta$ -Modifications of the Dithiocyanate-diamine Cupric Complex (and their E.S.D.)

Atom	$\alpha$ -Modification		$\beta$ -Modification		
	co-ordinates	temp. factor, $\text{\AA}^2$ <sup>a</sup>	co-ordinates	temp. factor, $\text{\AA}^2$ <sup>b</sup>	
Cu	$x/a$	0.1763 (3)	0.416	0.1763 (8)	1.60
	$y/b$	0.2500		0.2500	
	$z/c$	0.1092 (5)		0.1081 (13)	
S(1)	$x/a$	0.1644 (6)	0.190	0.1661 (15)	1.60
	$y/b$	0.7655 (64)		0.7388 (88)	
	$z/c$	0.0866 (9)		0.0892 (24)	
S(2)	$x/a$	0.4561 (5)	0.398	0.4552 (14)	1.60
	$y/b$	0.7642 (46)		0.8178 (58)	
	$z/c$	0.1203 (9)		0.1236 (26)	
N(1)	$x/a$	0.0463 (18)	0.416	0.0546 (56)	1.60
	$y/b$	0.2482 (152)		0.3223 (69)	
	$z/c$	0.2012 (30)		0.2014 (90)	
N(2)	$x/a$	0.3085 (17)	0.354	0.3144 (69)	1.60
	$y/b$	0.2606 (143)		0.2505 (270)	
	$z/c$	0.0187 (30)		0.0096 (119)	
N(3)	$x/a$	0.2348 (19)	0.637	0.2446 (46)	1.60
	$y/b$	0.2537 (158)		0.2532 (232)	
	$z/c$	0.3116 (29)		0.2991 (68)	
N(4)	$x/a$	0.3766 (20)	0.795	0.3831 (56)	1.60
	$y/b$	0.7562 (211)		0.6852 (173)	
	$z/c$	0.4113 (32)		0.4142 (99)	
C(1)	$x/a$	0.2773 (22)	0.810	0.2752 (55)	1.60
	$y/b$	0.2544 (224)		0.2833 (288)	
	$z/c$	0.4275 (36)		0.4384 (91)	
C(2)	$x/a$	0.4055 (20)	0.060	0.4144 (68)	1.60
	$y/b$	0.7254 (127)		0.7565 (327)	
	$z/c$	0.2843 (32)		0.2831 (103)	

Isotropic temperature factors: <sup>a</sup> individual, <sup>b</sup> general.

for both the modifications and their orientation with respect to the diffraction plane (020), since the modifications of the dithiocyanate-diamine cupric complex have been indentified in the powder diffraction patterns by pronounced differences in the diffraction intensities (020)<sup>10</sup>.

The X-ray structure analysis showed, in agreement with the considerations in the paper<sup>10</sup>, that certain atoms have different distances from the diffraction plane discussed (020). *E.g.* the deviation of the sulphur atom in the thiocyanate group with monodentate bonds varies within 0.09 to 0.35 Å (E.S.D.  $\pm$  0.003 Å), and in that one with bridging bonds, the sulphur atom shifts by 0.02 to 0.09 Å (E.S.D.  $\pm$  0.003 Å). The deviation from the diffraction plane was also observed for the ammonia molecules, within the range 0.01 to 0.3 Å (E.S.D.  $\pm$  0.05 Å).

The deviation of the tridentate sulphur bond from the diffraction plane (020) in one of the Cu—S bond directions causes, however, a shortening of these bonds in one direction, and a lengthening in the opposite direction. *E.g.* the difference between the two discussed bond lengths for the same copper atom is 0.18 Å for the  $\alpha$ -modification and 0.06 Å for the  $\beta$ -modification. While the first case represents the different length of the Cu—S bonds, in the case of the  $\beta$ -modification, the differences lie within the standard deviation and both lengths can be considered equal. In the data on the crystal structure of the dithiocyanate-diamine cupric complex, published so far, these bonds are always considered to be equal. (In the paper<sup>11</sup>, the length of the Cu—S bond is given as 3.023 Å and in the paper<sup>13</sup>, as 3.050 Å). If the values<sup>11</sup> of the structure factors  $F_0$  were used and refined by the least-squares method according to a non-centrosymmetrical space group, the *R*-factor decreased from 0.15 to 0.13. It was found that the discussed Cu—S bond lengths were neither in this case equivalent, and their difference had the value of 0.20 Å. From comparison

TABLE III

Some Interatomic Angles (degrees) (and their E.S.D.) in the  $\alpha$ - and the  $\beta$ -Modifications of the Dithiocyanate-diamine Cuprix Complex

Complex	$\alpha$ -Modification	$\beta$ -Modification
S(1)—Cu—S(1)	170 (0.33)	169 (0.67)
N(4)—Cu—N(3)	177 (3.5)	169.5 (4.4)
NH <sub>3</sub> —Cu—NH <sub>3</sub>	178 (3.3)	170 (4.1)
N(4)—C(2)—S(2)	162 (7.9)	160 (11.8)
N(3)—C(1)—S(1)	178 (11.4)	159 (7.0)
Cu—N(4)—C(2)	169 (9.5)	165 (11.8)
Cu—N(3)—C(1)	174 (5.5)	168 (7.2)

of the interatomic distances (Table I), it follows that the lengths of the Cu—N(4) bond in the modifications differ by the value of 0.08 Å. These are bonds belong to atoms forming monodentate bonds to the thiocyanate group. The differences in these bonds are by one order greater than those of the interatomic distances in both modifications and the difference values are greater than the standard deviation values. Also the lengths of the bonds Cu—N(4) ( $1.98 \pm 0.04$  Å) and N(4)—C(2) ( $1.15 \pm 0.04$  Å) are different for the  $\alpha$ - and  $\beta$ -modifications, after the refinement of the  $F_0$  values for the literature<sup>11</sup>. As follows from the values in Table II, some standard deviations of the co-ordinates have relatively high values. This fact is especially shown in the large values of the bond angle standard deviations (Table III). It is interesting that high standard deviations were observed in the case of atoms bonded mainly in thiocyanate groups, without respect to the value of the  $R$ -factor of the solved crystal structure. Since the solution of the crystal structures has not been finished in one case, the part of the discussion dealing with the comparison of the interatomic distances has mainly an informative character and points out those places in the molecule or in the co-ordination polyhedron where there are differences in the interatomic distances greater than the standard deviation. The knowledge of these places makes it possible to study these substances by substantially more sensitive and less time-consuming physico-chemical methods, *e.g.* by infrared spectrophotometry or by electron paramagnetic resonance. These investigations will follow later. The X-ray structure analysis, however, showed that the different properties of the modifications are due to structural differences which are on the level of the inner sphere of the structure units. The different diffraction properties of the modifications, as presented in the literature<sup>8</sup>, are connected with the varying degree of deviation of the thiocyanate groups from linearity. It cannot be excluded that the observed degrees of deviation, together with the observed great differences in the bond angles and their standard deviations could in some way mirror the dynamic character of the molecules of the dithiocyanate-diamine cupric complex, which is in agreement with the general assumptions about the dynamic character of the co-ordination sphere of Cu(II) complexes<sup>19</sup>.

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Translated by M. Štulíková.