THE THIOCYANATE GROUP AS LIGAND IN COPPER COMPLEXES THE STRUCTURE OF THE DITHIOCYANATE ETHYLENEDIAMINE COPPER(II) COMPLEX

J. GARAJ[a], M. DUNAJ-JURČO[a] and O. LINDGREN[b]

[a] *Department of Inorganic Chemistry, Slovak Institute of Technology, Bratislava,*
[b] *Department of Inorganic Chemistry, Chalmers Institute of Technology, Gothenburg, Sweden*

Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.

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The method of X-ray structure analysis has been applied to determine the crystal structure of the complex $Cu(NCS)_2en$. The substance crystallizes in the orthorhombic system with the space group $Pn2_1a$, with the lattice parameters: $a = 24{\cdot}518 \pm 0{\cdot}008$, $b = 6{\cdot}018 \pm 0{\cdot}001$, $c = 12{\cdot}413 \pm 0{\cdot}003$ Å. The measured density is 1·67 g cm^{-3} and the calculated value for $z = 8$ is 1·74 g cm^{-3}. 949 intensity values have been photometrically measured. The structure was refined by the method of full matrix least squares, yielding the value 0·110 for the *R*-factor. The structure is polymeric and the chains are parallel to the *b*-axis. Two types of coordination polyhedrons occur around Cu(II) in the crystal. In both cases, the divalent copper is coordinated in a plane by the nitrogen atom of ethylenediamine (2·12—2·14 Å) and the nitrogen atoms from the two thiocyanate groups (1·99 and 2·01 or 2·01 and 2·05 Å). The planar coordination bonds are supplemented by the sulphur atoms from the SCN group to give deformed octahedral coordination (2·99 and 3·10 or 3·01 and 3·10 Å). Some of the thiocyanate groups form bridges, others are monodentately bonded.

It is well known that, in aqueous solutions of cupric salts, Cu(II) is reduced to Cu(I) in the presence of thiocyanate ions. The oxidation–reduction process is slowed down or completely stopped by addition of certain ligands to the system. Such ligands are ammonia, pyridine(py), ethylenediamine(en), *etc.*

The crystal structures of the substances $Cu(NH_3)_4(SCN)_2$ and $Cu(NH_3)(NCS)_2$ are known[1–3]. From pyridine complexes, the structure of the very stable compound $Cu(py)_2(NCS)_2$[4] is known, while the complex $Cu(py)(SCN)_2$ is very unstable. The preparation[5] and structure of the complex $Cu(en)_2(CSN)_2$[6] have been described in the literature. The present paper deals with the so far unpublished preparation and structure of the thiocyanate complex $Cu(NCS)_2en$.

By a suitable arrangement of experiments it is possible to enhance the oxidation–reduction process in systems similar to those from which the above complexes crystallize, and in this way to prepare certain crystalline cuprous–cupric complexes[7,8].

For example, from the system Cu(II)-NH_3–SCN^- it was possible to prepare a compound of the composition $Cu_2(NH_3)_3(NCS)_3$[9]. By substitution of ammonia in this system by ethylenediamine, the cuprous-cupric compound $Cu_2en(NCS)_3$ has been prepared, the structure of which is at present being studied.

EXPERIMENTAL AND RESULTS

The Preparation of the Crystals

The complex $Cuen(SCN)_2$ was prepared in the following way: to 30 ml of 1M-$Cu(NO_3)_2$, 2 ml of ethylenediamine were added and, with stirring, 15 ml of 2M-NH_4SCN. The precipitate formed was dissolved by the addition of concentrated ammonia. After six months standing, the crystals were filtered off, washed with a small amount of water and alcohol, and dried in the air. The light blue crystals are stable in the air, slightly soluble in water, and insoluble in acetone and alcohol. For $Cu(SCN)_2en$ (239·8) calculated: 26·54% Cu, 48·70% SCN, 20·00% C, 23·40% N, 3·34% H. found: 25·90% Cu, 47·63% SCN, 19·97% C, 23·70% N, 3·04% H. The determination of copper and thiocyanate was carried out according to the procedure given in the literature[10]. The elemental analysis of the crystals was done in the Department of Analytical Chemistry, Slovak Institute of Technology.

Basic Structural Data

$Cu(NCS)_2en$ shows orthorhombic symmetry. The following systematic absences were found: For the reflection system of the type hkO are present those $F(hkO)$ for which $h = 2n$; for the reflection of the type Okl are present those $F(Okl)$ for which $k + l = 2n$. From the conditions follow the two space groups: $Pnma$ (No 62) and $Pn2_1a$ (No 33)[11].

The determination of the unit cell parameters was based on the Guinier powder patterns (CuK_α). After refining the experimental data by the method of least squares[12], the following lattice parameters were obtained: $a = 24{\cdot}51 \pm 0{\cdot}008$ Å, $b = 6{\cdot}018 \pm 0{\cdot}001$ Å, $c = 12{\cdot}413 \pm 0{\cdot}003$ Å, $\alpha = \beta = \gamma = 90°$. The volume of the unit cell is $V = 1831{\cdot}56$ Å^3. The density, measured by the immersion method, (19°C, bromoform, acetone) is $\varrho_{exp} = 1{\cdot}67$ gcm^{-3}. The calculated value, based on 8 formula units per unit cell is $\varrho_c = 1{\cdot}74$ gcm^{-3}. The ratio of the lattice parameters is $a : b : c = 4{\cdot}074 : 1{\cdot}000 : 2{\cdot}062$.

X-Ray Collection and Solution of the Structure

Five layers were obtained in the direction of the axis of growth (b-axis), by the Weissenberg equiinclination photography, using a needleshaped crystal, sized 0·05 × 0·08 × 0·4 mm. To obtain the intensities of the hkO projection, a 0·07 × 0·12 × 0·11 mm. crystal was used. 949 observable intensities were measured photometrically and corrected for the Lorentz polarization factor. The effect of absorption was neglected.

The location of the maxima in the three-dimensional Patterson map indicates that the $Cu(NCS)_2en$ structure has basically central symmetry. All strong maxima

in the Patterson synthesis could be explained assuming that the copper atoms occupy two four-fold positions with y-coordinates equal to 1/4 or 3/4*b*, respectively. By interpretation of the Patterson synthesis, also the approximate coordinates of the three sulphur atoms were determined.

The crystal structure was solved by the method of successive approximations. The coordinates of the sulphur atoms determined by the Patterson synthesis were verified by the Fourier synthesis calculated with signs of the structural factors taken from the copper atoms. From further Fourier syntheses were derived the coordinates of all the atoms present in the structure of $Cu(NCS)_2en$.

For refining the crystal structure, the method of least squares was used with the program by Ganzel, Sparkson and Trueblood[13] modified by Lindgren, on the basis of a centrally sym-

TABLE I

The Precise Coordinates of the Independent Atoms of the $Cu(NCS)_2en$ Crystals in Fractional Coordinates ($\times 10^4$) and of the Isotropic Individual Temperature Factors *B*

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Cu 1	0 484 (1)[a]	2 494 (0)[a]	1 677 (3)[a]	1·70 (98)[a]
Cu 2	2 640 (1)	2 430 (24)	5 869 (3)	1·90 (9)
S 1	2 353 (3)	2 506 (44)	0 663 (6)	1·09 (13)
S 2	4 544 (2)	2 394 (36)	6 633 (5)	0·81 (14)
S 3	3 651 (3)	2 584 (44)	9 141 (6)	1·99 (16)
S 4	0 854 (8)	2 348 (89)	7 257 (15)	2·24 (41)
S 5	1 134 (5)	2 744 (49)	8 234 (11)	2·32 (30)
N 1	1 247 (10)	2 386 (116)	1 248 (19)	2·34 (55)
N 2	0 184 (9)	2 512 (111)	0 265 (19)	1·89 (46)
N 3	3 057 (9)	2 606 (123)	7 196 (19)	2·12 (51)
N 4	1 943 (9)	2 864 (70)	6 644 (20)	1·78 (56)
N 5	2 251 (9)	2 769 (85)	4 394 (19)	1·87 (58)
N 6	3 331 (10)	2 589 (119)	4 904 (20)	2·63 (56)
N 7	0 714 (8)	2 804 (75)	3 283 (18)	1·40 (53)
N 8	4 717 (11)	2 752 (96)	2 728 (22)	2·93 (67)
C 1	1 720 (12)	2 335 (145)	1 053 (25)	2·61 (70)
C 2	4 936 (10)	2 131 (78)	5 550 (20)	0·79 (57)
C 3	3 292 (9)	2 287 (92)	8 037 (18)	0·41 (49)
C 4	1 455 (18)	2 105 (139)	6 866 (36)	1·37 (98)
C 5	2 662 (15)	2 971 (91)	3 552 (28)	3·30 (89)
C 6	3 145 (13)	1 899 (67)	3 777 (26)	2·11 (81)
C 7	0 231 (12)	2 052 (87)	3 954 (26)	2·39 (82)
C 8	4 824 (14)	3 195 (69)	1 458 (31)	3·28 (90)
C 9	1 623 (16)	2 927 (105)	7 391 (36)	0·47 (93)

[a] Standard deviations are given in parentheses.

TABLE II

The Found and the Calculated Values of the Structural Factors for the Compound $Cu(SCN)_2en$

h 0 l	F_o	F_c
4 0 0	159·9	189·2
8	30·1	41·1
10	152·6	183·3
12	42·4	46·3
14	75·6	92·5
16	49·7	42·0
18	44·2	32·9
22	109·8	96·1
26	52·4	38·9
28	75·0	70·8
0 0 2	35·1	34·2
4	149·8	180·9
8	113·7	112·0
12	121·6	125·0
1 0 1	94·9	111·4
2	83·4	104·6
3	4·4	19·9
4	77·4	77·2
5	115·2	105·8
6	142·7	153·4
7	89·0	90·1
8	61·8	61·6
9	63·1	19·5
10	63·1	53·6
11	96·6	90·8
12	125·3	131·4
13	34·3	31·5
14	61·6	56·6
15	138·9	128·9
16	124·9	113·2
17	148·5	131·4
20	66·9	56·4
21	84·6	83·9
22	22·6	30·1
23	26·1	29·3
24	38·1	40·7
25	65·2	70·6
26	67·0	66·5
1 0 2	95·8	120·8
2	145·5	149·6
3	39·4	41·8
4	87·1	85·1
5	212·1	242·6
7	70·9	56·2
8	170·3	168·8
9	100·4	92·7
11	68·4	56·1
12	82·4	79·9
14	50·9	37·1
15	96·4	96·9
17	72·6	67·9

h 0 l	F_o	F_c
19	52·0	45·3
20	55·7	51·3
23	42·6	50·4
24	73·5	39·9
1 0 3	73·6	93·2
2	136·2	127·8
3	70·2	55·4
5	37·1	43·5
6	34·9	27·1
7	98·4	84·0
8	50·8	43·1
9	69·9	64·1
10	196·9	173·8
11	155·8	156·0
12	127·5	114·2
13	135·3	131·0
14	130·7	116·8
15	34·3	30·1
16	67·2	56·8
17	62·3	52·3
18	92·4	94·5
19	74·4	72·4
20	73·3	80·0
21	63·7	73·8
22	45·5	38·4
23	55·8	54·8
24	39·0	24·4
26	39·7	41·5
1 0 4	43·9	49·4
2	27·0	22·3
3	164·7	181·3
4	54·0	52·0
5	27·5	22·9
6	84·2	68·7
7	161·5	187·2
8	47·2	32·4
9	21·8	20·5
10	113·6	93·0
11	60·8	45·1
12	75·6	66·9
13	150·7	141·5
14	37·6	33·2
15	45·4	37·2
16	63·7	48·6
17	45·6	47·4
19	98·2	92·9
22	50·9	53·8
25	68·4	75·6
1 0 5	84·9	87·4
3	89·6	84·8
4	117·7	180·4

h 0 l	F_o	F_c
5	36·9	30·3
6	41·4	45·1
7	93·3	73·6
8	125·8	124·6
9	76·6	66·9
10	89·5	89·1
11	34·0	29·6
13	134·4	125·3
14	113·9	104·3
16	41·6	35·4
17	61·5	60·5
18	102·9	115·5
19	77·5	72·2
22	45·4	52·8
23	57·1	50·1
24	51·2	51·6
25	36·4	33·3
1 0 6	7·2	6·9
2	185·1	206·2
3	30·8	21·7
4	41·5	50·1
6	45·2	46·7
8	164·3	178·2
10	33·3	20·2
12	121·8	108·8
14	49·0	44·7
18	59·3	68·1
20	50·7	80·2
24	42·7	49·7
1 0 7	68·9	65·9
4	110·9	122·3
5	61·9	65·4
6	119·7	118·5
7	52·9	40·5
8	79·2	74·3
9	99·9	98·9
10	53·9	47·4
11	28·2	16·9
13	72·4	70·0
14	56·6	43·4
15	59·8	38·9
16	44·5	35·9
17	43·7	36·8
18	70·9	64·1
19	59·2	59·8
23	69·8	89·5
24	65·3	47·3
25	40·3	27·8
1 0 8	52·1	46·5
3	154·3	139·1
4	57·8	54·6

h 1 l	F_o	F_c
6	83·4	69·6
7	133·4	145·4
8	26·0	22·6
10	70·2	63·1
11	60·6	56·5
13	75·8	74·8
15	42·1	33·9
19	40·6	41·9
22	29·5	42·7
23	34·5	26·8
26	37·0	25·9
1 0 9	87·2	83·5
2	60·3	46·8
3	96·3	81·5
4	61·8	54·3
5	29·0	24·9
6	32·8	37·3
7	33·1	25·6
8	29·8	26·2
9	24·1	35·8
10	55·8	40·6
11	81·3	82·2
13	35·1	31·0
14	51·9	60·0
16	42·6	43·4
17	39·1	31·4
18	32·6	61·1
19	45·9	48·9
20	46·2	55·9
21	53·9	61·2
22	38·8	22·8
23	36·5	39·8
1 0 10	56·7	46·4
2	80·4	63·0
3	48·2	44·2
4	43·4	36·8
5	149·6	130·1
7	31·3	41·8
8	44·6	37·3
9	65·5	55·7
11	32·1	43·8
12	45·5	34·8
15	63·7	62·9
17	48·4	55·8
18	33·5	26·0
20	27·6	33·7
2 0 11	27·6	33·7
4	42·3	51·9
6	66·2	69·4
7	60·2	57·6
11	47·8	34·0

TABLE II
(*Continued*)

h *l* *l*	F_o	F_c
12	72·9	76·0
15	76·1	65·4
16	65·7	67·3
17	40·7	41·1
6 0 12	103·4	53·3
4 0 13	51·3	58·4
6	40·4	50·4
7	42·7	40·2
11	43·7	53·1
12	27·9	30·2
1 0 14	28·7	34·9
2	43·0	49·3
5	72·4	71·9
7	34·4	38·6
8	18·9	31·9
2 1 0	51·3	47·2
4	125·9	142·5
6	17·4	15·3
8	31·8	26·0
10	42·3	41·8
12	13·8	15·6
14	54·3	57·7
16	26·6	14·8
18	48·1	46·4
20	49·7	60·5
0 1 3	30·5	24·0
5	68·1	71·3
7	71·0	71·5
9	88·8	93·0
13	34·6	35·4
1 1 1	47·9	46·4
2	144·6	126·7
3	107·0	134·9
4	98·2	90·2
5	83·4	82·9
6	16·7	13·0
7	14·1	13·1
8	43·7	48·6
9	52·1	43·6
10	67·9	52·5
11	43·4	41·2
12	45·5	37·2
13	59·8	54·5
14	18·9	7·7
15	24·9	20·7
18	31·9	27·8

h *l* *l*	F_o	F_c
1 1 2	47·9	50·0
2	100·1	82·1
3	115·1	99·5
4	36·7	33·2
5	23·8	17·2
6	64·9	60·5
7	57·8	43·7
8	26·3	9·4
9	98·6	104·5
10	47·3	32·6
11	24·7	24·2
12	53·3	53·1
13	50·8	62·6
14	15·9	26·8
15	50·8	51·4
23	47·3	50·6
1 1 3	17·8	8·8
2	24·4	11·0
3	68·3	81·0
4	28·1	31·3
5	53·5	42·0
6	36·5	44·7
7	26·6	17·8
8	85·4	86·9
9	38·1	33·5
10	65·0	63·9
12	26·4	20·1
13	30·9	28·2
14	28·4	22·5
15	54·3	56·5
16	26·5	27·3
17	55·4	62·9
18	34·4	22·9
19	28·7	34·2
25	36·1	43·9
1 1 4	20·4	21·8
2	26·8	22·8
3	45·8	45·7
5	80·1	77·2
6	18·2	10·4
7	69·4	72·3
8	58·0	50·5
9	22·0	22·1
10	52·0	47·7
11	33·8	34·2
12	48·9	48·2
13	34·7	31·7
14	54·4	63·1
15	39·9	50·1
17	25·6	26·3
18	20·5	31·1
19	18·0	21·8

h *0* *l*	F_o	F_c
20	43·6	47·5
21	35·1	38·6
22	26·5	22·1
2 1 5	42·1	42·8
3	69·7	64·4
4	20·3	11·7
5	106·6	123·0
6	15·8	9·1
7	22·7	29·1
8	5·9	22·3
9	37·2	38·9
10	38·7	37·2
13	41·4	38·5
14	18·4	23·6
15	39·7	40·2
16	30·1	34·4
17	43·1	39·5
18	6·0	0·4
22	28·4	21·4
2 1 6	84·9	77·2
3	52·2	46·5
4	43·0	41·9
5	14·4	14·1
6	24·4	23·0
9	21·6	14·4
10	62·3	64·8
11	21·7	19·0
12	48·4	46·9
13	33·6	33·8
14	44·5	59·1
15	44·1	51·6
18	32·9	27·4
20	36·7	30·3
22	44·4	46·8
2 1 7	19·4	16·7
4	56·2	60·4
5	78·0	73·5
6	75·3	79·5
9	15·8	9·5
10	74·4	83·2
11	18·9	17·6
12	15·2	9·0
13	18·4	18·7
14	27·1	22·9
2 1 8	17·2	20·0
3	24·2	16·5
4	28·0	16·0
6	49·7	47·6
7	73·3	67·8
8	29·3	20·7

h *0* *l*	F_o	F_c
9	17·4	14·2
10	17·9	11·3
11	37·4	38·6
12	23·9	20·0
13	20·4	13·9
14	21·0	9·6
15	45·6	38·6
16	34·4	36·4
17	37·7	41·5
21	49·8	40·1
23	34·8	47·0
1 1 9	40·9	43·4
2	46·1	47·3
5	51·8	54·9
8	68·7	68·1
9	27·8	23·8
10	22·7	22·2
2 1 10	40·0	35·5
4	45·2	36·7
8	30·0	28·7
9	37·4	38·6
10	28·5	17·4
11	25·5	30·3
12	49·7	51·6
13	24·1	22·6
15	41·1	34·9
16	36·3	36·7
17	12·6	12·0
18	29·9	33·0
19	30·0	15·1
20	28·9	30·6
21	26·8	34·7
3 1 11	58·0	67·1
5	34·7	37·4
6	37·9	41·6
7	43·1	35·0
8	18·8	13·9
9	26·4	17·6
10	34·0	25·0
12	14·0	6·6
15	17·6	10·5
6 1 12	28·2	25·3
7	26·1	31·0
9	27·8	34·1
10	45·6	46·4
11	20·4	18·0
12	28·5	32·0
13	25·9	22·0
14	32·9	30·1
15	26·1	29·5

TABLE II

(*Continued*)

h *0* *l*	F_o	F_c
2 1 13	80·8	69·9
8	58·6	61·4
0 2 0	543·8	633·3
2	19·9	29·0
4	119·6	141·8
6	63·0	60·9
8	30·1	32·1
10	143·3	163·7
12	45·8	45·0
14	84·0	78·5
16	40·7	35·5
18	33·2	31·9
22	85·4	90·6
24	18·2	7·8
26	37·5	35·3
28	58·1	63·9
0 2 2	22·0	29·0
4	120·1	137·8
8	99·7	103·6
12	104·7	114·8
1 2 1	75·1	91·7
2	80·2	89·8
3	31·4	25·4
4	51·6	60·8
5	86·6	85·6
6	111·4	134·1
7	66·1	76·9
8	59·3	56·0
10	60·6	55·4
11	84·5	82·9
12	116·8	109·5
13	33·2	28·9
14	57·4	48·8
15	112·6	113·9
16	109·5	102·2
17	108·3	113·9
20	51·8	52·8
21	65·2	74·9
22	29·8	29·3
23	32·3	28·2
24	32·8	37·0
25	52·6	63·8
26	56·1	62·2
1 2 2	103·5	109·6
2	115·5	122·5
3	36·5	37·3
4	68·5	66·6
5	190·2	205·7
7	54·5	55·8
8	131·8	137·6

h *1* *l*	F_o	F_c
9	71·3	79·6
11	52·3	55·8
12	65·1	68·6
14	28·3	31·6
15	80·6	88·9
17	59·8	64·4
19	44·3	41·0
20	48·5	46·7
23	49·0	46·3
24	34·1	37·4
25	22·9	24·3
27	74·9	88·1
1 2 3	103·9	89·1
3	67·4	57·4
4	18·6	20·7
5	30·2	31·3
6	26·5	26·3
7	70·7	66·0
8	43·4	41·9
9	55·0	62·0
10	137·4	143·3
11	125·7	131·0
12	94·7	98·9
13	106·9	113·5
14	98·2	100·0
15	28·9	26·0
16	58·4	51·3
17	43·4	43·5
18	82·5	86·4
19	66·0	66·6
20	75·0	74·5
21	68·5	65·5
22	45·1	37·4
23	42·4	49·7
24	30·6	22·1
1 2 4	43·9	45·4
2	18·9	18·0
3	157·8	159·2
4	53·7	40·1
5	26·4	18·1
6	67·7	62·1
7	147·0	157·4
8	30·3	27·7
10	91·5	84·9
11	42·3	36·3
12	59·6	58·7
13	120·7	125·1
14	34·9	30·5
15	37·2	35·3
16	43·9	40·5
17	42·8	44·2
19	86·7	83·9

h *1* *l*	F_o	F_c
22	52·9	49·1
25	61·8	69·8
1 2 5	70·8	72·7
2	26·6	30·5
3	67·9	68·2
4	156·5	148·5
5	27·0	27·2
6	51·1	47·7
7	68·2	60·2
8	102·7	107·2
9	62·4	62·7
10	63·8	74·7
11	36·5	24·1
13	116·7	110·9
14	95·5	92·6
15	59·2	58·6
16	36·5	31·3
17	64·5	53·3
18	101·5	102·2
19	71·3	65·0
20	23·8	19·6
22	39·5	45·4
23	49·8	46·5
24	52·2	48·4
25	35·1	30·0
2 2 6	173·9	179·8
3	17·5	17·4
4	37·8	44·8
5	27·2	24·9
6	44·2	42·7
8	161·2	156·8
10	35·0	24·5
12	92·2	98·4
14	37·6	41·3
17	28·1	27·3
18	62·3	62·5
20	68·8	73·7
24	49·9	47·4
1 2 7	66·6	62·0
4	104·2	107·6
5	60·0	55·6
6	103·7	103·5
7	49·3	38·5
8	78·1	66·3
9	94·7	88·4
13	63·2	66·8
14	47·1	41·8
15	50·4	37·5
16	40·2	33·6
17	49·4	36·8
18	69·1	58·8

h *2* *l*	F_o	F_c
19	53·8	55·5
23	66·6	81·9
1 2 8	42·6	39·1
3	132·9	122·1
4	50·5	50·7
6	61·5	59·5
7	117·2	125·6
9	49·4	43·9
10	59·4	58·2
11	43·0	45·9
13	74·2	70·0
17	30·6	27·6
18	30·6	28·1
19	45·2	38·8
1 2 9	77·3	78·5
2	46·8	40·1
3	72·9	71·7
4	49·3	47·6
5	22·9	21·5
6	32·3	29·5
7	31·5	26·6
8	28·1	25·8
9	40·1	33·7
10	52·1	36·2
11	79·4	74·6
12	61·4	62·4
13	31·9	29·5
14	51·5	52·2
15	33·2	30·4
16	51·5	40·5
17	34·0	29·8
18	54·7	54·1
19	42·3	43·0
20	55·9	51·0
21	49·0	57·7
1 2 10	54·6	42·7
2	65·7	56·9
3	43·6	38·3
4	36·6	32·4
5	123·5	118·7
7	38·2	35·7
8	38·3	35·0
9	47·4	51·8
11	40·4	40·6
12	38·3	32·9
15	56·5	56·9
17	58·7	52·5
18	25·5	23·6
19	35·7	31·6
20	34·0	33·7

TABLE II
(*Continued*)

h	*k*	*l*	F_o	F_c
6	2	11	53·4	64·6
7			63·7	54·6
8			16·2	7·2
10			39·2	32·6
11			33·2	31·4
12			76·6	69·3
14			19·5	15·8
15			63·8	58·9
16			64·1	62·1
17			43·4	37·5
10	2	12	96·0	86·1
12			45·2	41·6
0	3	1	22·0	24·4
		3	5·0	10·5
		5	38·5	41·2
		7	68·3	64·7
		9	70·3	66·6
2			28·6	32·9
4			82·7	97·0
6			26·8	27·1
8			21·1	23·1
10			38·3	33·6
12			8·3	18·2
14			38·8	38·2
16			20·6	27·4
18			28·6	28·8
20			35·1	45·6
1	3	1	12·5	22·2
2			61·7	82·0
3			70·3	86·3
4			40·3	49·4
5			50·5	50·6
7			15·0	17·6
8			38·3	43·4
9			33·0	31·4
10			49·7	41·3
11			32·1	29·8
12			37·0	31·1
13			46·5	41·4
15			10·0	16·8
18			32·4	24·8
2	3	2	49·1	52·9
3			46·0	35·0
4			32·1	27·1
5			19·1	20·3
6			35·7	30·7
7			43·3	36·8
8			13·0	9·9
9			66·1	69·8
10			26·1	21·2
11			20·7	27·3
12			38·2	36·3
13			42·1	40·5
14			21·6	22·8
15			44·3	40·1
17			10·7	13·6
22			10·9	9·7
23			30·1	37·9
3	3	3	44·1	54·9
4			31·4	33·7
5			28·1	19·5
6			20·8	30·0
7			18·3	18·6
8			63·3	61·9
9			22·1	21·1
10			46·9	46·0
11			17·0	13·9
12			24·0	17·6
13			27·6	24·2
14			28·1	16·0
15			57·9	46·4
16			30·7	21·6
17			51·6	46·4
18			27·9	25·6
19			31·2	24·9
21			10·9	10·7
26			28·5	12·0
1	3	4	17·0	27·5
2			16·1	15·3
3			34·9	35·3
5			51·9	47·8
6			14·1	14·6
7			54·5	54·9
8			46·5	38·1
9			24·1	23·8
10			49·6	38·3
11			22·5	21·4
12			48·3	37·5
13			33·5	25·0
14			50·3	46·5
15			35·7	36·0
18			11·0	20·5
19			11·0	20·3
20			36·6	39·6
21			26·6	25·9
22			10·7	15·4
2	3	5	26·8	29·6
3			47·7	45·2
4			7·9	14·3
5			100·3	88·9
7			27·6	26·1
8			22·2	21·0
9			33·9	27·3
10			34·7	34·1
13			31·0	29·9
14			21·1	20·3
15			31·4	30·0
16			30·9	26·5
17			38·2	34·8
20			11·0	14·4
21			11·0	19·4
22			11·0	16·0
23			9·9	11·5
24			9·8	16·0
2	3	6	63·1	58·9
3			27·8	23·3
4			40·1	33·1
6			9·0	17·0
7			9·5	15·7
9			10.0	9·6
10			67·7	53·5
11			17·8	18·8
12			44·3	38·9
13			32·0	27·6
14			42·0	46·6
15			41·1	41·4
18			11·0	23·9
19			29·7	16·6
20			11·0	21·5
2	3	7	24·8	16·5
4			51·5	46·7
5			64·5	51·0
6			65·0	58·4
10			65·4	61·5
12			10·8	9·1
13			11·0	13·7
14			11·0	17·2
22			31·5	24·1
2	3	8	10·2	14·2
3			11·0	17·3
5			52·3	50·1
6			44·4	34·9
7			63·6	50·7
15			31·9	30·5
16			36·0	31·0
17			31·1	33·2
21			38·6	31·3
1	3	9	32·2	35·7
2			38·8	39·3
5			45·4	45·0
8			58·3	52·6
2	3	10	29·3	29·3
4			35·8	28·0
8			24·7	23·2
9			32·1	29·6
10			27·8	19·5
11			31·5	24·7
12			35·5	40·6
14			29·1	20·5
15			29·2	27·4
16			33·5	29·0
3	3	11	47·2	56·6
5			31·1	30·4
6			31·1	31·8
7			34·1	30·9
15			20·1	6·5
10	2	12	36·1	37·0
11			13·1	14·2
12			28·3	24·5
10	3	13	25·8	17·7
4	4	0	60·6	81·3
6			58·7	62·7
10			138·3	124·0
12			37·0	39·2
14			50·9	53·5
18			22·8	27·3
22			57·2	75·3
0	4	4	78·9	79·8
		8	79·3	82·9
1	4	1	51·0	59·6
2			59·7	64·5
4			43·9	36·6
5			59·8	55·7
6			106·4	96·7
7			56·5	57·1
8			53·9	43·7
9			18·1	14·8
10			48·3	45·9
11			66·1	64·3
12			78·4	72·0
14			39·9	33·9
15			82·2	84·2
16			69·6	80·5
17			69·7	79·2
20			34·5	43·3
21			41·6	55·8
1	4	2	72·7	82·1
2			83·6	81·6

TABLE II
(*Continued*)

h 4 *l*	F_o	F_c
4	49·5	40·2
5	141·6	146·1
7	42·6	41·9
8	97·0	89·4
9	56·9	56·6
11	46·1	45·0
12	50·0	47·7
15	68·0	70·3
17	45·3	52·4
20	35·2	36·2
23	29·8	36·4
1 4 3	63·2	72·0
2	64·6	59·5
3	57·8	50·6
4	23·7	21·3
5	22·3	15·8
6	23·8	20·6
7	47·9	41·0
8	37·4	35·8
9	51·1	53·2
10	96·9	92·8
11	94·4	87·4
12	69·7	70·6
13	85·2	80·8
14	73·9	67·8
16	42·9	39·1
17	22·8	26·1
18	63·2	67·2
19	51·6	52·8
20	48·0	60·7
21	44·7	48·3
22	39·7	33·0
23	29·9	38·5

h 2 *l*	F_o	F_c
1 4 4	33·8	35·9
3	119·7	119·6
4	27·8	22·9
6	50·4	44·5
7	114·9	106·4
10	76·0	66·6
11	27·6	22·8
12	49·7	43·0
13	91·5	92·4
14	31·5	23·8
15	35·6	29·7
16	41·0	25·1
17	37·7	35·7
19	61·6	62·7
1 4 5	48·4	49·2
2	26·3	26·3
3	43·2	43·7
4	112·3	96·8
5	28·3	20·5
6	52·0	44·6
7	47·4	38·8
8	85·1	75·3
9	53·4	50·6
10	48·1	49·2
13	88·1	80·9
14	71·1	69·9
15	39·5	47·5
16	25·5	23·8
17	40·6	38·3
18	70·7	74·4
19	46·6	48·8
24	34·0	40·3

h 3 *l*	F_o	F_c
2 4 6	138·1	129·8
4	31·1	30·9
6	35·9	34·6
8	128·2	114·4
10	32·1	27·0
12	80·5	74·8
14	36·8	33·1
15	25·4	19·6
18	45'2	49·0
20	51·1	57·6
1 4 7	51·7	50·5
4	67·2	78·1
5	45·1	37·9
6	83·5	75·0
7	38·2	32·7
8	56·7	49·0
9	76·8	67·0
13	52·1	56·2
14	30·9	36·0
15	34·3	32·6
17	31·1	33·4
18	51·0	46·0
19	40·2	44·9
1 4 8	22·2	24·8
3	94·5	88·5
4	48·0	41·0
5	19·4	10·3
6	42·3	41·2
7	85·5	86·7
9	33·1	31·1
10	42·6	46·9
11	34·9	26·3
12	15·9	18·6

h 3 *l*	F_o	F_{c0}
13	57·3	56·8
1 4 9	60·2	63·7
2	31·1	27·2
3	54·5	51·5
4	32·2	33·9
8	19·9	22·8
9	29·6	28·6
10	32·4	26·7
11	55·1	57·9
12	44·7	50·2
13	27·0	24·7
14	29·8	35·9
15	30·8	23·9
16	27·8	33·1
17	25·9	24·7
18	37·6	39·1
19	31·8	29·7
1 4 10	42·1	34·1
2	33·8	44·0
3	19·9	26·0
4	25·0	22·6
5	83·5	92·1
6	24·8	11·6
7	19·9	22·7
8	30·7	28·4
9	38·0	42·2
11	26·0	32·7
12	31·1	28·2
13	31·8	6·5
0 6 0	167·3	169·4
4	59·8	48·0
8	15·1	20·3

metrical space group; the reliability factor obtained was 0·13. The Fourier synthesis showed that the electron densities corresponding to the atoms S_4 and C_4 are only one half of those for the other sulphur and carbon atoms. As can be seen from Fig. 1, there are other similar maxima for S_5 and C_9 in the vicinity of the above atomic positions. The nitrogen atom is shared by both S—C couples. The Fourier synthesis, in which the S_4 and C_4 atoms were replaced by the S_5 and C_9 atoms, did not lead to the removal of splitting of the S_4—C_4—N_4 group. If first S_4—C_4 and then S_5—C_9 were assigned weights for whole atoms, identical values of the R factor were obtained, $R = 0{\cdot}160$. In further calculations, S_4 and C_4, and S_5 and C_9 atoms were assigned half the values of the weight of positional factors. Finally, all atomic coordinates were refined according to the $P\,n\,2_1\,a$ space group yielding the value $R = 0{\cdot}110$, defined as $\sum||F_o| - |F_c|| : \sum|F_o|$. Besides the atomic positions, the scale factors of layers and the isotropic temperature coefficients were refined. For refinement of the structure, the Cruickshank weighting scheme was

used[13], where $w\Delta^2 = \text{const.}$, and $w = (A + F_0 + CF_0^2)^{-1/2}$. The A and C constants had final values of 20·0 and 0·006, respectively. The atomic factor curves used in the calculations agree with those Ibers[14].

The process of refining the results was completed by Fourier synthesis. The maximum electron density in the differential map attained the value 1·65 e/Å^3, at the position of the nitrogen atoms of the ethylenediamine molecule, and is probably chiefly caused by the hydrogen atoms which were not considered in the calculations.

The resulting fractional coordinates of the atoms of the independent part of the unit cell are given together with the standard deviations and temperature coefficients in Table I. The observed and calculated structure factors are listed in Table II.

DISCUSSION

The calculations of interatomic distances, bond angles, and standard deviations for the precise structure of $Cu(NCS)_2en$ were carried out using the program of Zalkin, as modified by Lindgren. The results of the calculations are given in Table II.

In the crystal structure of the dithiocyanate–ethylenediamine cupric complex, shown by Figs 1 and 2, there are two symmetrically independent Cu(II) atoms around

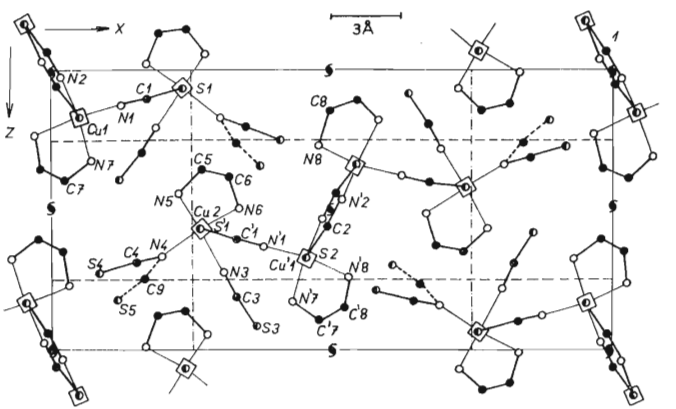

FIG. 1

The Projection of the Structure in the Direction of the *y*-Axis

The atomic positions denoted by a symbol without a dash are identical with the data in Tables I and II; the symbols with a dash denote symmetrically dependent positions. □ Cu, ◐ S, ● C, ○ N.

which are formed two symmetrically independent complex units. The type of coordination to the central atom is identical for both the symmetrically independent positions Cu(1), and Cu(2), and the interatomic metal-to-ligand distances also have close values. The divalent copper atom forms strong, basically covalent bonds to the nitrogen atoms of the thiocyanate groups, with interatomic distances Cu—N = 1·99 and 2·01 Å, or 2·01 and 2·05 Å (Tables II and III). The interatomic distances of the copper and the nitrogen atoms of the ethylenediamine molecules are evidently greater. They have the values 2·12 and 2·14 Å, or 2·14 and 2·14 Å for the other independent coordination polyhedron. The two sulphur atoms are located at greater distances from the central atom. The interatomic distances Cu—S are not identical in either of the two polyhedrons (2·99 and 3·10 Å, or 3·01 and 3·10 Å). The difference in the interatomic distances is significant when it approaches the value 0·1 Å as in the case of the Cu—N bonds and when it exceeds the standard deviation values (Tables II, III, Fig. 2).

Comparing the lengths of the chemical bonds Cu-ligand, found in the structure solution of $Cu(NCS)_2en$, with the data found for other thiocyanate complexes of divalent copper, (Table IV), good agreement is found, generally within the value

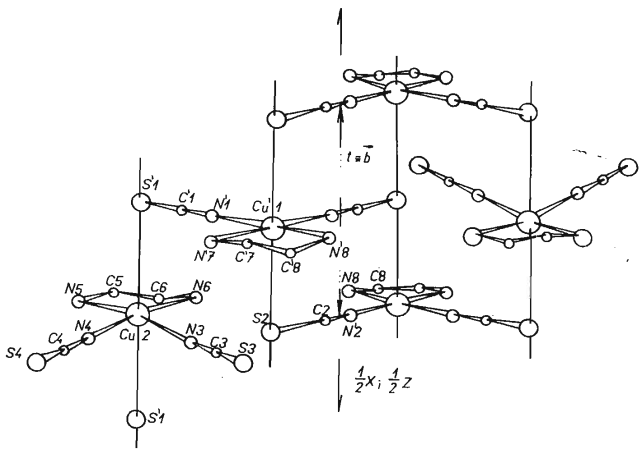

FIG. 2

A Polymeric Complex Unit in a Schematic Spatial Picture (a tetramer within the frame of the *b*-translation)

The atoms are denoted in agreement with Tables I and II and with Fig. 1.

TABLE III

The Interatomic Angles and Distances in the Crystals of the Complex $Cu(NCS)_2en$

Atomic group	Angles °	Distances, Å
	The coordination polyhedron around Cu (1)	
S 2 — Cu 1 — S 2	176·5 (0·3)[a]	Cu 1 — N 2 1·99 (2)[a]
S 2 — Cu 1 — N 1	91·3 (2·2)	Cu 1 — N 1 2·01 (2)
S 2 — Cu 1 — N 2	87·3 (1·8)	Cu 1 — N 8 2·12 (3)
S 2 — Cu 1 — N 7	97·0 (1·2)	Cu 1 — N 7 2·14 (2)
S 2 — Cu 1 — N 8	94·6 (1·3)	Cu 1 — S 2 2·99 (2)
S 2 — Cu 1 — N 1	90·7 (2·2)	Cu 1 — S 2 3·10 (2)
S 2 — Cu 1 — N 2	89·7 (1·8)	
S 2 — Cu 1 — N 7	86·9 (1·2)	
S 2 — Cu 1 — N 8	83·7 (1·3)	
N 1 — Cu 1 — N 2	96·8 (1·0)	
N 1 — Cu 1 — N 7	90·0 (0·9)	
N 1 — Cu 1 — N 8	171·8 (1·9)	
N 2 — Cu 1 — N 7	172·4 (1·2)	
N 2 — Cu 1 — N 8	89·2 (1·0)	
N 7 — Cu 1 — N 8	83·7 (1·0)	
	The coordination polyhedron around Cu(2)	
S 1 — Cu 2 — S 1	170·1(0·3)	CS 2 — N 3 2·01 (3)
S 1 — Cu 2 — N 3	97·8 (1·8)	Cu 2 — N 4 2·05 (2)
S 1 — Cu 2 — N 4	99·9 (1·0)	Cu 2 — N 5 2·14 (2)
S 1 — Cu 2 — N 5	90·9 (1·3)	Cu 2 — N 6 2·14 (2)
S 1 — Cu 2 — N 6	98·8 (1·7)	Cu 2 — C 6 2·99 (4)
S 1 — Cu 2 — N3	90·3 (1·8)	Cu 2 — S 1 3·01 (2)
S 1 — Cu 2 — N 4	85·5 (1·0)	Cu 2 — S 1 3·10 (2)
S 1 — Cu 2 — N 5	80·6 (1·3)	
S 1 — Cu 2 — N 6	84·0 (1·7)	
N 3 — Cu 2 — N 4	91·5 (1·0)	
N 3 — Cu 2 — N 5	170·3 (2·0)	
N 3 — Cu 2 — N 6	93·7 (1·0)	
N 4 — Cu 2 — N 5	91·1 (0·9)	
N 4 — Cu 2 — N 6	168·3 (1·8)	
N 5 — Cu 2 — N 6	82·1 (0·9)	
	Thiocyanate group 1	
Cu 2 — S 1 — Cu 2	170·1 (0·3)	S 1 — C 1 —1·68 (3)[a]
Cu 2 — S 1 — C 1	85·9 (3·0)	C 1 — N 1 1·25 (4)
Cu 2 — S 1 — C 1	92·0 (3·0)	

TABLE III
(*Continued*)

Atom	Angles °	Distances, Å
Cu 1 — N 1 — C 1	175·0 (6·0)	
Cu 2 — S 1 — N 1	89·0 (1·6)	
Cu 1 — N 1 — S 1	179·3 (1·9)	
S 1 — C 1 — N 1	172·3 (1·9)	
	Thiocyanate group 2	
S 2 — C 2 — N 2	165·0 (4·0)[a]	S 2 — C 2 1·71 (3)[a]
Cu 1 — N 2 — C 2	169·0 (3·6)	C 2 — N 2 1·24 (4)
Cu 1 — S 2 — C 2	86·0 (1·5)	
Cu 1 — S 2 — C 2	97·4 (1·5)	
	Thiocyanate group 3	
Cu 2 — N 3 — C 3	165·4 (4·7)[a]	S 3 — C 3 1·69 (2)[a]
S 3 — C 3 — N 3	161·2 (4·0)	C 3 — N 3 1·29 (3)
	Thiocyanate group 4	
S 4 — C 4 — N 4	154·7 (4·9)[a]	S 4 — C 4 1·65 (4)[a]
Cu 2 — N 4 — C 4	149·8 (3·2)	C 4 — N 4 1·32 (5)
	Thiocyanate group 4′	
S 5 — C 9 — N 4	168·2 (3·9)[a]	S 5 — C 9 1·63 (4)[a]
Cu 2 — N 4 — C 9	157·8 (2·6)	C 9 — N 4 1·28 (5)
	Ethylenediamine molecule 1	
Cu 2 — N 5 — C 5	110·5 (1·8)[a]	N 5 — C 5 1·50 (4)[a]
Cu 2 — N 6 — C 6	105·3 (2·0)	C 5 — C 6 1·46 (5)
N 5 — C 5 — C 6	111·6 (3·1)	C 6 — N 6 1·59 (5)
N 6 — C 6 — C 5	108·7 (3·2)	
	Ethylenediamine molecule 2	
Cu 1 — N 7 — C 7	108·8 (1·8)[a]	N 7 — C 7 1·55 (4)[a]
Cu 1 — N 8 — C 8	103·1 (2·0)	C 7 — C 8 1·37 (6)
N 8 — C 8 — C 7	117·0 (3·7)	C 8 — N 8 1·64 (6)
N 7 — C 7 — C 8	105·0 (3·4)	

of the standard deviation. Anomalously large values for the length of the Cu—NCS bond (2·10 Å), found in the compound $Cu(NCS)_2py_2$, may be due to the fact that the structural parameters were obtained on the basis of the isomorphism of the above complex with the Cobalt(II) compound of the same formula, probably without refinement of the structure[4].

The thiocyanate group, which is bonded to the central metal atom through the nitrogen, is, according to its position in the spectrophotometric series, a ligand producing a stronger field than an ammonia or amine nitrogen. Generally, the Cu—NH_3 chemical bond is longer than the Cu—NCS one[1]. In the $Cu(NCS)_2$en structure, the difference in the lengths of these bonds is a marked one and verifies the above conclusion.

The ethylenediamine molecules form chelates with the central atom. The chemical bond lengths and bond angles in this molecule are close to those found in other crystal structures[6,15–17]. The molecule is not planar: both carbon atoms deviate in opposite directions from a plane drawn through the nitrogen atoms and the Cu(II)

TABLE IV

The Lengths of the Chemical Bonds Cu-Ligand

Composition	*a*	*b*	*c*	*d*	*e*	*f*
$Cu(NH_3)_2(NCS)_2$	$L_1 = L_2$ 2 . Cu—NH_3 = 2·00 2 . Cu—NH_3 = 1·98	2 . Cu—S = 3·03	*trans*	2	1	1; 2
$Cu(NH_3)_4(SCN)_2$	$L_1 = L_2$ 4 . Cu—NH_3 = 1·98	2 . Cu—S = 3·00	—	2	2	3
$Cu_2(NH_3)_3(NCS)_3$[g]	$L_1 \neq L_2$ 3 . Cu—NH_3 = 2·04	1 . Cu—S = 2·95	—	1	1	19
$Cupy_2(NCS)_2$	$L_1 = L_2$ 2 . CuN(py) = 2·12	2 . Cu—S = 3·02	*trans*	2	2	4
$Cu(SCN)_2\overset{\frown}{en}_2$	$L_1 = L_2$ 4 . Cu—NH_2 = 2·00	2 . Cu—S = 3·27	*cis*	2	2	6
$Cu(NCS)_2$en	$L_1 \neq L_2$ 2 . Cu—NH_2 = 2·13 2 . Cu—N = 2·00	1 . Cu—S = 2·99 1 . Cu—S = 3·10	*cis*	2	1	—
$Cu(NCS)_2$en	$L_1 \neq L_2$ 2 . Cu—NH_2 = 2·14 2 . Cu—N = 2·03	1 . Cu—S = 3·01 1 . Cu—S = 3·10	*cis*	2	1	—
$CuHg(SCN)_4$	$L_1 = L_2$ 4 . Cu—N = 1·95	2 . Cu—S = 3·02	—			16; 17

[a] The equivalence of the lengths of sulphur atoms bonded on the long coordinates in octahedral coordination, [b] the interatomic distance Cu-ligand, [c] the mutual location of the nitrogen ligands in the squareplanar base of the deformed octahedron, [d] the number of coordinated SCN groups in the coordination polyhedron through nitrogen or sulphur, [e] the number of noncoordinated nitrogen atoms or sulphur atoms from the thiocyanate groups, [f] literature, [g] the situation with the cuprous–cupric complex is more complicated since each SCN group functions as a bridge. The data in this line refer only to the bonds of SCN to Cu(II).

atom. The chemical bond lengths and the bonding angles between the atoms in the thiocyanate groups are shown in Table II.

TABLE V

Intermolecular Contacts for $Cu(NCS)_2en$ Shorter than 3·3 Å

Atom	Distance, Å	Atom	Distance, Å
N 3 — C' 1	3·28 (10)[a]	S 4 — C 8	3·23 (6)
N 6 — C' 1	3·25 (10)	S 4 — N 8	3·21 (7)
N 2 — N' 2	3·26 (2)	S 5 — C 6	3·20 (5)
N 2 — C' 2	2·85 (8)	C 4 — C 6	3·10 (7)

[a] Standard deviations in parentheses.

The structure of $Cu(NCS)_2$ is based on tetramers composed of two symmetrically independent types of distorted octahedrons (Figs 1, 2). In the direction of the *b*-axis, the tetrameric units are linked by weaker copper-sulphur bonds into infinite chains, parallel to the *b*-axis. The formation of infinite chains enables the thiocyanate groups to act as bridges. In crystals of $Cu(NCS)_2$, all the SNC groups are coordinated to the central atom through nitrogen atoms, but only one half of the thiocyanate groups are additionally bonded to the central atom through the sulphur atom. These bridging SCN groups, which are tridentate, are bonded, along with the nitrogen atoms, to a single central atom; in Figs 1 and 2, this is the Cu(1) atom. The thiocyanate groups coordinated to the Cu(2) atom through nitrogen atoms are monodentate.

The copper atoms deviate from a plane drawn through the nitrogen ligands in the direction to the nearer sulphur atom. The equations for these planes for both types of polyhedrons, calculated by the method of least squares are given by:

$$0{\cdot}0265X + 0{\cdot}9976Y - 0{\cdot}0641Z = 1{\cdot}4886\,, \qquad (1)$$

$$0{\cdot}0391X + 0{\cdot}9992Y - 0{\cdot}0039Z = 1{\cdot}8943\,, \qquad (2)$$

where X, Y, Z are orthogonal coordinates in Å. The atomic deviations (Å) from these planes are: *1*. Cu = −0·076; N_1 = 0·020; N_2 = 0·021; N_7 = 0·021; N_8 = = 0·022. *2*. Cu = −0·1735; N_3 = 0·009; N_4 = 0·009; N_5 = −0·009; N_6 = 0·009. It is not uninteresting that identical Cu—S distances have also been found in the crystals of the complex $Cu_2(NCS)_3(NH_3)_3$ (see[18]) and that they are not rare in the structures of cupric compounds.

One of the monodentate thiocyanate groups occupies a statistical position in the structure of $Cu(NCS)_2$, while the nitrogen atom position is practically unchanged. During the refinement process, both the S—C positions were assigned a 50% positional factor. The interatomic distances are, within the standard deviation value, identical in both S—C—N group positions (Table II). The closest atoms in both positions of the S—C group approach the van der Waals interaction distance (Table V).

In Table IV are given some data on all the so far known thiocyanate cupric structures. A property common to all of these structures is the approximately planar arrangement of the nitrogen atoms which can be considered necessary as a condition for the redox stability of divalent copper. The sulphur atoms coordinated to Cu(II) are located at distances which, in the case of symmetrically drawn out systems, do not fall below 3·0 Å, and, in the case of an assymmetrical arrangement of sulphur atoms on the longest coordinate, are further than 2·95 Å from the central atom. The preferential occupation of these coordinates by sulphur atoms rather than by nitrogen atoms, even in structures containing sufficient numbers of nitrogen atoms to form a homogeneous coordination sphere, is apparently due to the effect of the central atom which, having d^9 electron configuration in the valence sphere, has a tendency to produce deformed coordination systems.

It is interesting that, if SCN groups coordinate divalent copper also through the sulphur atoms, then these sulphur atoms are regularly bound to two copper atoms, while the other atoms remain free.

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REFERENCES

1. Garaj J.: Ž. Strukt. Chim. *7*, 727 (1966).
2. Garaj J.: Chem. zvesti *17*, 488 (1963).
3. Poraj-Košic M. A., Tiščenko G. N.: Kristallografija *4*, 240 (1959).
4. Poraj-Košic M. A.: Ž. Strukt. Chim. *4*, 384 (1963).
5. Grossman H., Schuck B.: Z. Anorg. Chem. *50*, 1 (1906).
6. Brown B., Lingafelter L. C.: Acta Cryst. *17*, 254 (1965).
7. Dunaj-Jurčo M., Poraj-Košic M. A.: Chem. zvesti *20*, 241 (1966).
8. Brajbanti A., Tiripiccio A.: *Tezisy Dokladov VII. Meždunarodnogo Kongresa IUC*, p. 129. Moscow 1966.
9. Garaj J.: Z. Chem. (*1965*), 430.
10. Garaj J.: Chem. zvesti *17*, 488 (1963).
11. *International Tables for X-Ray Crystallography*, Vol. I. The Kynoch Press, Birmingham 1962.
12. Linquist O., Wengelin F.: Arkiv Kemi *28*, 179 (1967).

13. Cruikshank D. W. J., Pilling D. E., Sujosa A., Lovell F. M., Truter M. R.: *Computing Methods and the Phase Problem in X-Ray Analysis*, p. 32. Symposium Publications Division, Pergamon Press, New York 1961.
14. Ibers I. A.: *International Tables for X-Ray Crystallography*, Vol. III, p. 202. Kynoch Press, Birmingham 1962.
15. Korczynski A. in the book: *Theory and Structure of Complex Compound*, p. 405. (B. Jezowska-Trzebiatowska, Ed.) Pergamon Press, Oxford; Wyd. Nauk.-Techn., Warsawa 1964.
16. Poraj-Košic M. A.: Ref. 15, p. 137.
17. Dunaj-Jurčo M., Poraj-Košic M. A.: Chem. zvesti *21*, 241 (1967).
18. Garaj J.: Inorg. Chem. *8*, 304 (1969).

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