

Temperature influence on the crystal structure of the mixed valence copper cyanide complex $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$

Z. KOŽÍŠKOVÁ, M. DUNAJ-JURČO, and † J. GAŽO

*Department of Inorganic Chemistry, Slovak Technical University,
CS-812 37 Bratislava*

Received 20 September 1982

Accepted for publication 3 October 1983

An investigation of the low-temperature (148 K) influence on the crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ in which two coordination polyhedra of Cu(II) and Cu(I) are present was carried out. Decrease of the temperature has shown significant differences of the bond distances in the coordination polyhedron of Cu(II) being in good agreement with the conception of its plasticity.

Изучалось влияние низкой температуры (148 K) на кристаллическую структуру $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$, в которой находятся два координационных полиэдра Cu(I) и Cu(II). Понижение температуры появилось на валентных расстояниях в координационном полиэдре Cu(II), что соответствует представлению об его пластичности.

Generalization of the results of a great many Cu(II) coordination compound investigations, for which the considerable variability of the bond distances central atom—ligand is typical, yielded the discovery of phenomenon of the distortion isomerism of Cu(II) complexes [1], further the knowledge of expressive plasticity of Cu(II) coordination polyhedra [2, 3], and the knowledge of equatorial—axial interaction of ligands in the coordination polyhedron of Cu(II) [4]. In this connection the influence of temperature on the crystal structures of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ [5] and $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ was investigated.

Experimental

The crystals of complex $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ with known crystal structure [6] were prepared according to the literature [8]. Three structure determinations at the temperatures of 298 K, 148 K, and again 298 K were carried out.

The basic crystallographic data were verified by the oscillation and the Weissenberg photographic technique at the temperature of 298 K with Weissenberg camera VBG2 (Freiberger Präzisionmechanik) and at the temperature of 148 K, using the Nonius low-temperature apparatus.

The density of the crystals was measured by the flotation method in a $\text{CHBr}_3/\text{CH}_3\text{CH}_2\text{OH}$ mixture. The basic crystallographic data are given in Table 1.

Table 1

Crystal data for $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ at different temperatures

Formula	$\text{Cu}_5\text{N}_{10}\text{C}_6\text{H}_{12}$		
Cell dimensions at	298 K	148 K	298 K
a/pm	766.1(4)	749.3(6)	764.5(7)
b/pm	890.0(4)	892.1(5)	890.3(5)
c/pm	1372.6(6)	1362.0(10)	1370.0(10)
$\beta/^\circ$	126.06(4)	125.85(6)	126.18(6)
$V(\text{calc.})/\text{m}^3$	756.6×10^{-30}	738.1×10^{-30}	752.8×10^{-30}
$\rho(\text{found})$	2.38 g cm^{-3}		
$\rho(\text{calc.})$	2.38 g cm^{-3}		
Z	2		
Space group	$P 2_1/c$		
$F(000)$	526		
$\mu(K_\alpha(\text{Mo}))$	71.8 cm^{-1}		

Table 2

Conditions of intensity data collection

Radiation	$\lambda(K_\alpha(\text{Mo})) = 71.069 \text{ pm}$		
Monochromator	Graphite		
Crystal dimensions	$0.1 \text{ mm} \times 0.5 \text{ mm} \times 0.2 \text{ mm}$		
Scan mode	$\Theta: 2\Theta$		
Scan speed/($^\circ/\text{min}$)	4.88—29.3		
Scan range	$\pm 1^\circ$ from the peak centre		
Background count	1/2 of the reflection scan time at each end of the scan		
Check reflections	2 every 98 reflections, no decay		
Data collection limits	$0 < 2\Theta < 55^\circ$		
	$h, k, \pm l$		
Temperature	298 K	148 K	298 K
Number of data collected	1615	1587	1607
with $I > 1.96 \sigma(I)$	1028	1128	963

The needle-shaped crystal of dimensions $0.1 \text{ mm} \times 0.5 \text{ mm} \times 0.2 \text{ mm}$ was sealed along the b axis on a glass fibre; intensity data were collected at the temperatures of 298 K, 148 K, and 298 K.

The unit cell dimensions were determined using least-squares procedures for the angular positions of 10 selected reflections from a rotation polaroid photograph obtained from the four-circle automatic diffractometer Syntex P2₁. The temperature of 148 K was maintained using the Syntex LT-1 low-temperature attachment. The gaseous nitrogen cooled by liquid nitrogen was used as cooling medium at a flow of $15 \text{ cm}^3 \text{ s}^{-1}$. The temperature was measured before and after experiment by thermocouple.

Conditions of integral intensity data collection are listed in Table 2. The intensities of independent diffractions were corrected for Lorentz and polarization factors. The empirical absorption correction was made using six empirical absorption curves with the values 2Θ : 9.86° , 12.01° , 18.92° , 21.39° , 25.48° , and 28.07° . Each curve goes through 36 points (rotation angle Θ varied by 10°) of the measured intensity as a function of the rotation angle Θ .

Structure refinement

Atomic coordinates for the nonhydrogen atoms [6] were used in the refinement by full-matrix least-squares method. The final values of R in anisotropic refinement are given in Table 3. The results of difference Fourier synthesis showed the maximum residual electron density to be $0.4 \text{ e}^-/10^{-30} \text{ m}^3$.

The positional and thermal parameters of the nonhydrogen atoms with the estimated standard deviation are listed in Tables 4–7. The interatomic distances and bond angles with their estimated standard deviations are shown in Table 8.

All programs used were from an XTL program system supplied by Syntex Corporation.

Table 3

The R value for observed diffractions ($I > 1.96 \sigma(I)$) at different temperatures

Temperature	298 K	148 K	298 K
R_1	0.055	0.061	0.057
R_2	0.050	0.058	0.049

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}, \text{ where } w = 1/\sigma^2, \sigma^2 = [(F_o - \sigma(I)/L_p)^{1/2} - F_o]$$

Table 4

Fractional coordinates of atoms (x, y, z) with esd's in parentheses at different temperatures

Atom	298 K			148 K			298 K		
	10 ⁴ x	10 ⁴ y	10 ⁴ z	10 ⁴ x	10 ⁴ y	10 ⁴ z	10 ⁴ x	10 ⁴ y	10 ⁴ z
Cu(1)	0	0	0	0	0	0	0	0	0
Cu(2)	2659(3)	957(1)	4723(1)	2625(3)	976(2)	470(1)	2660(3)	957(2)	4725(1)
Cu(3)	7402(2)	932(1)	1861(1)	7431(3)	950(2)	1872(1)	7408(3)	933(2)	1863(1)
C(1)	2424(17)	3024(11)	4248(8)	2388(20)	3034(12)	4241(9)	2381(19)	3027(12)	4230(9)
C(2)	7518(17)	2911(11)	1430(8)	7552(20)	2946(12)	1440(8)	7525(19)	2912(12)	1430(8)
N(3)	2433(16)	4218(9)	4004(7)	2430(18)	4243(10)	4000(8)	2424(17)	4223(10)	4002(8)
N(4)	7471(15)	4116(10)	1090(7)	7510(18)	4139(11)	1101(8)	7482(17)	4110(11)	1088(8)
D(5)	2943(16)	4649(10)	1182(8)	2882(18)	4619(10)	1153(9)	2911(19)	4650(10)	1174(9)
D(6)	7060(16)	160(10)	3018(9)	7091(18)	159(11)	3039(10)	7067(18)	169(11)	3022(10)
N(7)	1749(14)	1259(8)	1546(7)	1770(16)	1255(9)	1547(7)	1733(15)	1257(8)	1548(7)
N(8)	7632(14)	3427(8)	4169(7)	7618(16)	3441(9)	4179(7)	7632(16)	3439(9)	4171(7)

D — nitrogen or carbon atom of disordered cyanide group.

Table 5

Numerical values of anisotropic temperature parameters ($B_{ij}/(10^{-22} \text{ m}^2)$) with esd's in parentheses at 298 K

Atom	$\{B_{11}\}$	$\{B_{22}\}$	$\{B_{33}\}$	$\{B_{12}\}$	$\{B_{13}\}$	$\{B_{23}\}$
Cu(1)	343(10)	152(6)	276(8)	5(8)	170(8)	14(6)
Cu(2)	570(9)	204(5)	440(7)	19(6)	340(7)	27(5)
Cu(3)	456(8)	211(5)	422(7)	-37(6)	311(7)	-18(5)
C(1)	276(58)	258(43)	306(49)	76(45)	167(46)	- 28(39)
C(2)	309(61)	247(44)	206(43)	1(42)	124(43)	- 25(34)
N(3)	461(57)	257(40)	334(41)	-37(41)	222(41)	- 29(34)
N(4)	450(56)	393(45)	299(39)	-26(45)	227(40)	- 79(38)
D(5)	596(65)	292(43)	509(52)	21(43)	395(53)	22(37)
D(6)	628(66)	298(43)	655(57)	-95(47)	454(54)	-202(42)
N(7)	398(50)	225(36)	300(39)	4(35)	182(39)	- 45(29)
N(8)	434(53)	208(35)	303(41)	-76(37)	184(40)	- 29(29)

Temperature parameters are in the form

$$T_i = \exp [-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

Table 6

Numerical values of anisotropic temperature parameters ($B_{ij}/(10^{-22} \text{ m}^2)$) with esd's in parentheses at 148 K

Atom	$\{B_{11}\}$	$\{B_{22}\}$	$\{B_{33}\}$	$\{B_{12}\}$	$\{B_{13}\}$	$\{B_{23}\}$
Cu(1)	233(11)	64(6)	163(8)	8(7)	117(8)	11(6)
Cu(2)	366(9)	103(5)	266(7)	7(6)	214(7)	15(5)
Cu(3)	297(8)	102(5)	253(7)	-23(6)	199(6)	- 21(5)
C(1)	284(66)	181(44)	157(48)	37(47)	165(49)	- 6(39)
C(2)	198(60)	165(42)	76(41)	-24(40)	119(43)	- 33(33)
N(3)	318(58)	186(42)	178(41)	6(41)	147(42)	0(34)
N(4)	351(59)	227(44)	217(42)	-25(44)	206(43)	71(37)
D(5)	431(67)	161(39)	326(49)	- 2(41)	285(51)	25(35)
D(6)	488(70)	140(40)	508(57)	-35(46)	375(56)	-107(41)
N(7)	203(48)	76(34)	165(37)	13(32)	81(36)	6(28)
N(8)	275(54)	100(34)	192(42)	-13(36)	142(41)	2(30)

Table 7

Numerical values of anisotropic temperature parameters ($B_{ij}/(10^{-22} \text{ m}^2)$) with esd's in parentheses at 298 K
(after the change from 148 K to 298 K)

Atom	$\{B_{11}\}$	$\{B_{22}\}$	$\{B_{33}\}$	$\{B_{12}\}$	$\{B_{13}\}$	$\{B_{23}\}$
Cu(1)	445(12)	147(7)	306(9)	6(9)	232(9)	12(7)
Cu(2)	673(11)	196(6)	466(8)	12(7)	398(8)	29(6)
Cu(3)	557(10)	208(6)	449(7)	– 35(7)	373(8)	– 17(6)
C(1)	424(74)	238(46)	295(53)	42(51)	243(55)	33(41)
C(2)	475(78)	224(47)	216(47)	– 44(48)	217(52)	– 40(36)
N(3)	500(65)	309(46)	343(44)	– 18(46)	225(46)	– 6(38)
N(4)	594(68)	389(49)	334(43)	– 45(51)	311(47)	– 94(41)
D(5)	832(82)	268(45)	551(57)	80(49)	527(62)	34(40)
D(6)	831(83)	295(47)	759(67)	–105(55)	606(67)	–185(47)
N(7)	440(57)	183(37)	315(42)	– 63(37)	225(43)	– 80(30)
N(8)	513(63)	214(39)	304(45)	– 96(41)	214(46)	– 9(32)

Table 8

Numerical values of the interatomic distances (d/pm) and of the changes of distances (Δ_{ij}/pm) with esd's in parentheses at different temperatures

Atom	1st experiment at 298 K	Change of distance { $\Delta_{2,1}$ }	2nd experiment at 148 K	Change of distance { $\Delta_{3,2}$ }	3rd experiment at 298 K
Cu(1)—N(7)	205.1(7)	—0(1)	204.8(8)	0(1)	204.4(8)
Cu(1)—N(8)	202.9(9)	—2(1)	201.0(10)	1(1)	202.3(10)
Cu(1)—C(1)	314.0(13)	—7(2)	307.9(15)	5(2)	312.2(14)
Cu(1)—N(3)	297.1(12)	—6(2)	291.2(14)	5(2)	296.0(14)
Cu(2)—C(1)	192.4(10)	—0(2)	192.1(19)	0(2)	193.0(11)
Cu(2)—N(4)	195.2(9)	—1(2)	194.0(12)	1(2)	195.2(10)
Cu(2)—D(5)	195.8(10)	—2(2)	194.3(12)	1(2)	195.6(12)
Cu(2)—C(2)	317.7(14)	—4(2)	314.0(16)	3(2)	316.7(14)
Cu(2)—N(4)	299.5(10)	—2(2)	297.1(15)	2(2)	299.2(11)
Cu(3)—C(2)	187.7(10)	2(2)	189.2(11)	—2(2)	187.7(11)
Cu(3)—N(3)	198.2(9)	—0(1)	197.8(10)	0(1)	198.0(10)
Cu(3)—D(6)	188.5(12)	0(2)	188.4(13)	0(2)	188.2(13)
C(1)—N(3)	111.6(13)	2(2)	113.6(14)	—2(2)	111.6(14)
C(2)—N(4)	116.2(14)	—1(2)	115.2(14)	1(2)	115.7(14)
D(5)—D(6)	119.0(15)	0(2)	119.4(17)	—1(2)	188.5(17)

Structure description

In the crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ there are two coordination polyhedra of Cu(I), labelled as Cu(2) and Cu(3) (Figs. 1 and 2) and a coordination polyhedron of Cu(II), labelled as Cu(1).

The cation of Cu(II) (Cu(1)) lies in the origin of unit cell, *i.e.* in the symmetry centre, a special position of space group $P 2_1/c$ and it is pseudo-octahedrally coordinated. The equatorial plane is formed by four nitrogen atoms of NH_3 ligands. In the axial positions the centres of triple cyanide bond are found to form two-dimensional network.

The coordination geometries around the cations of Cu(I) (Cu(2), Cu(3)) are approximately trigonal-planar and they consist of carbon and nitrogen atoms from two ordered and one disordered cyanide groups.

The cyanide groups appear as bidentate ligands bonded terminally to the two Cu(I) cations.

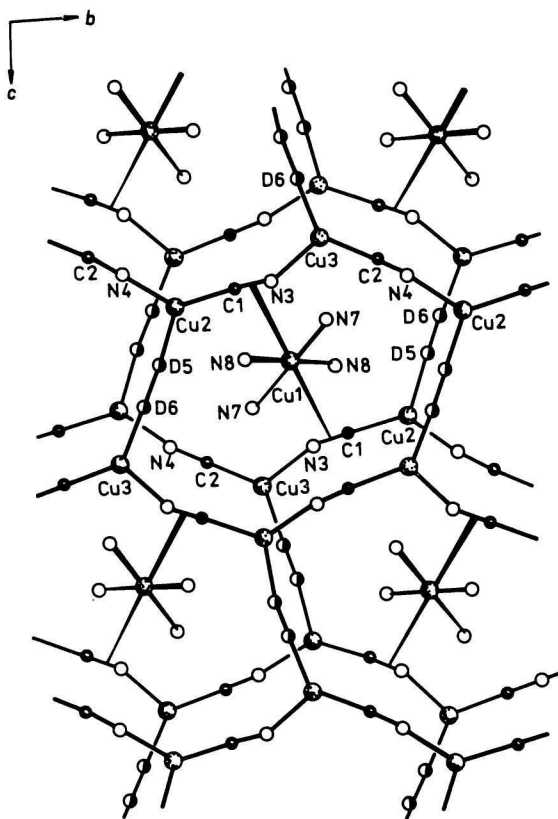


Fig. 1. The crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$.

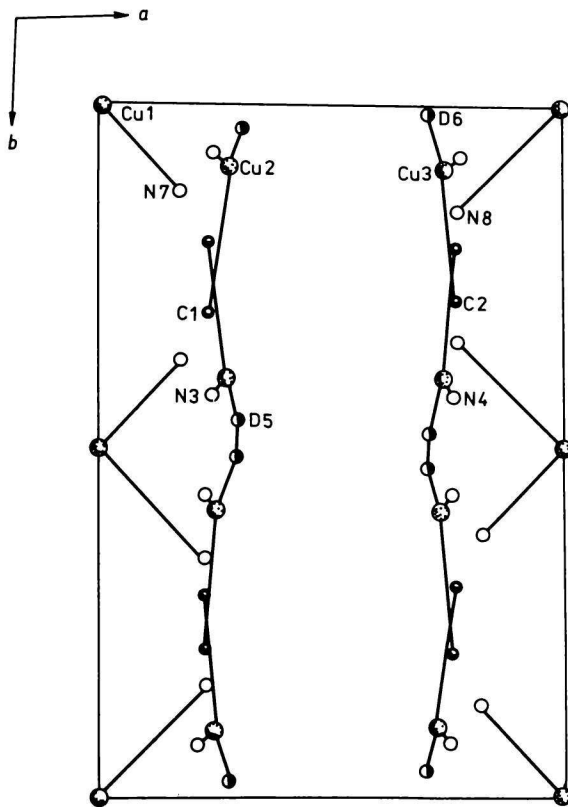


Fig. 2. Projection of unit cell down c .

The layer crystal structure consists of two-dimensional infinite sheets formed by six-membered rings of the composition of $[\text{Cu}_{2n}(\text{CN})_{3n}]^{n-}$. These layers are parallel (100) with heights $x = 0.25$ and $x = 0.75$. As it is shown in Fig. 2 the empty space between polymeric $[\text{Cu}_{2n}(\text{CN})_{3n}]^{n-}$ anions is to a half occupied by $[\text{Cu}(\text{NH}_3)_4]^{2+}$ cations. This formation consisting of the three sheets (one cationic and two anionic) may be written as $[\text{Cu}(\text{NH}_3)_4]_n^{2+}[\text{Cu}_{2n}(\text{CN})_{3n}]_2^{n-}$.

Discussion

The coordination geometries of two symmetrically independent cations of Cu(I) are trigonal-planar with interatomic distances: Cu(I)—C 188(1) pm and 192(1) pm, Cu(I)—N 195.2(9) pm and 198.2(9) pm, Cu(I)—D (D means the nitrogen or carbon atom of disordering cyanide group) 196(1) pm and 189(1) pm, respectively. Similar coordination geometry of Cu(I) cation is also in crystal

structures of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ [5, 6, 9] and $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ [10] in which analogous interatomic distances have similar values.

The bonding angles of Cu(I) coordination polyhedra are in the range of 106° and 132° (Table 9). This range contains values of analogous angles found in crystal structures of $[\text{Cu}(\text{NH}_3)_3][\text{Cu}_2(\text{CN})_4]$ [11], $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ [10], and $\text{KCu}(\text{CN})_2$ [12].

Table 9

Interatomic angles with esd's in parentheses at different temperatures

Bonds	Angle/ $^\circ$		
	298 K	148 K	298 K
N(7)—Cu(1)—N(8)	88.4(4)	88.9(4)	88.7(4)
D(5)—Cu(2)—N(4)	106.9(4)	106.4(5)	106.5(5)
N(4)—Cu(2)—C(1)	130.2(5)	131.0(5)	130.3(5)
C(1)—Cu(2)—D(5)	122.8(5)	122.5(5)	123.0(5)
D(5)—Cu(2)—N(4)	106.9(4)	106.4(5)	106.5(5)
D(6)—Cu(3)—C(2)	131.6(5)	131.6(5)	131.4(5)
C(2)—Cu(3)—N(3)	120.1(5)	120.8(5)	120.1(5)
N(3)—Cu(3)—D(6)	108.3(5)	107.6(5)	108.5(5)
Cu(3)—N(4)—C(2)	169.7(10)	170.1(11)	170.3(11)
Cu(2)—C(2)—N(4)	175.6(10)	175.5(11)	170.5(11)
Cu(2)—D(5)—D(6)	171.8(10)	171.2(11)	172.2(11)
Cu(3)—D(6)—D(5)	173.5(10)	172.7(11)	172.8(11)
Cu(3)—N(3)—C(1)	157.9(10)	158.5(11)	157.7(11)
Cu(2)—C(1)—N(3)	175.2(11)	174.2(12)	173.5(12)

One from the two independent Cu(I) coordination polyhedra is completed by the centre of cyanide group triple bond to a trigonal-planar polyhedron through the vacancy not occupied by cations. The bond distance of Cu(2)—centre of the triple bond is 309(1) pm (Table 8). The cations Cu(2) and Cu(3) do not lie precisely on the triangle plane formed by C, N, and D atoms (Table 10).

The copper(II) cation (Cu(1)) is pseudo-octahedrally coordinated. The equatorial plane is formed by nitrogen atoms of NH_3 with interatomic distances of Cu(1)—N 205.1(7) pm and 202.9(9) pm; these values being common in ammine copper(II) complexes [5, 6]. The coordination geometry is completed in axial positions at the distance of 306(1) pm by the centre of the triple bond of two cyanide groups originated from adjacent anionic sheets (Figs. 1 and 2, Table 8).

Two thirds of the cyanide groups using their π donor ability take part in forming the π complex [7] with cations Cu(I) and Cu(II). This fact was also confirmed by quantum chemistry calculations [13].

Table 10

Equation of planes and deviation of atoms with esd's in parentheses at different temperatures

Plane	Atoms	θ/K	Deviation/pm	Equation of plane
1	Cu(1), N(7), N(8)	298		$0.8258x - 0.4513y - 0.3381z = -7.2203$
		148		$0.8298x - 0.4449y - 0.3368z = -7.1871$
		298		$0.8260x - 0.4533y - 0.3350z = -7.2222$
2	Cu(1), C(1), N(3)	298		$-0.4114x - 0.1499y - 0.8991z = -3.9933$
		148		$-0.4155x - 0.1384y - 0.8990z = -3.8184$
		298		$-0.4086x - 0.1327y - 0.9030z = -3.9215$
3	Cu(2)	298	-2.2 (2)	$-0.8623x - 0.0329y - 0.5053z = -1.1202$
	C(1)		0.8(13)	
	N(4)		0.7(12)	
	D(5)		0.7(13)	
4	Cu(3)	298	1.3(2)	$-0.7408x - 0.0113y - 0.6717z = -2.0073$
	C(2)		-0.5(12)	
	N(3)		-0.4(11)	
	D(6)		-0.4(12)	
The angle between planes 1 and 2 at		298 K	88°	
		148 K	89°	
		298 K	89°	

The cyanide group appears as a bridging ligand and *via* nitrogen and carbon atom produces two terminal σ bonds with copper(I) cations and the creation of the two-dimensional polymeric anion, which is the characteristic building element of the structure is conditioned by this fact.

The atoms of cyanide groups do not lie in the straight line going through the Cu(I) cations. The angles Cu(I)—C—N, Cu(I)—N—C, and Cu(I)—D—D differ from the value of 180° by no more than 10° except the angle Cu(3)—N(3)—C(1) being $158(1)^\circ$ and this cyanide group is the one coordinating the Cu(II) cation by the π bond. The bond Cu(II)—centre of cyanide group triple bond is almost perpendicular to the equatorial plane of Cu(II) polyhedron. The angle between the equatorial plane of Cu(II) coordination polyhedron and the plane going through atoms Cu(1), C(1), and N(3) is 88° (Table 10).

Similar value of angles was found in the crystal structure of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})] \cdot [\text{Cu}_2(\text{CN})_4]$ [9], in which two types of cyanide group are present. 1. Two Cu(I) cations are connected by two cyanide groups and 2. two Cu(I) cations are connected by one cyanide group. In case 2. it may be observed that the cyanide group, the centre of triple CN bond of which is found in axial position of Cu(II) is attracted to the Cu(II) coordination polyhedron (the angles Cu(I)—C—N and Cu(I)—N—C are $173(1)^\circ$) and the cyanide group which is not in direct interaction with Cu(II) coordination polyhedron is turned away (the angles Cu(I)—C—N and Cu(I)—N—C are $186(1)^\circ$ and $189(1)^\circ$, respectively).

The investigation of temperature influence on the crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ shows that with decreasing temperature from 298 K to 148 K no phase transition occurs. The crystal keeps the same symmetry (Table 1). The change of temperature was manifested by changes in lattice parameters and interatomic distances (Table 8).

The axial π bond between Cu(II) and centre of triple CN bond was changed from 306(1) pm to 299(1) pm. The difference represents 7(2) pm. A similar situation was found in the case of low-temperature experiment with the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})] \cdot [\text{Cu}_2(\text{CN})_4]$ complex, where just the value of axial interatomic distances of Cu(II) coordination polyhedron was changed [5]. The other interatomic distances and angles remained almost unchanged (Tables 8 and 9). The angle between planes 1 and 2 remained unchanged, too (Table 11). This points to the fact that the sheets of polymeric anions $[\text{Cu}_{2n}(\text{CN})_{3n}]^{n-}$ were attracted through the empty space occupied by cations (Fig. 2) in the direction of axis x . It was the lattice parameter a which was with decreasing temperature most expressively changed.

The results of the third experiment at a temperature of 298 K are almost the same and thus the changes found in this crystal structure, due to changes of temperature, may be considered as reversible.

The results obtained by comparison of changes due to decreasing temperature from 298 K to 148 K in crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ with changes due to decreasing temperature from 298 K to 173 K in the crystal structure of

Table 11

Numerical values of the van der Waals bonds (d/pm) with esd's in parentheses in crystal structure of $[\text{Cu}(\text{NH}_3)_4][\text{Cu}_4(\text{CN})_6]$ at different temperatures

Atoms	Bonds through the vacancy not occupied by cations		Bonds through the vacancy occupied by cations	
	298 K	148 K	298 K	148 K
C(1)—C(2)	334(2)	333(2)	346(2)	339(2)
Cu(2)—D(6)	—	—	354(1)	343(2)

$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ point to the fact that the coordination polyhedron of Cu(II) undergoes more easily the changes. This fact is in good agreement with the conception of the plasticity of Cu(II) coordination polyhedron compared with that of Cu(I).

References

1. Gažo, J., *Pure Appl. Chem.* 38, 279 (1974).
2. Gažo, J., Bersuker, I. B., Garaj, J., Kabešová, M., Kohout, J., Langfelderová, H., Melník, M., Serátor, M., and Valach, F., *Coord. Chem. Rev.* 19, 253 (1976).
3. Gažo, J., Kabešová, M., Valach, F., and Melník, M., *Koord. Khim.* 2, 715 (1976).
4. Gažo, J., Boča, R., Jóna, E., Kabešová, M., Macášková, L., Šima, J., Pelikán, P., and Valach, F., *Coord. Chem. Rev.* 43, 87 (1982).
5. Kožíšek, J., CSc. Thesis. Slovak Technical University, Bratislava, 1981.
6. Dunaj-Jurčo, M., *Habilitation Thesis*. Slovak Technical University, Bratislava, 1973.
7. Dunaj-Jurčo, M., Lingafelter, E. C., Gažo, J., Garaj, J., *Proc. IV Conf. Coord. Chem.*, p. 21. Smolenice—Bratislava, 1973.
8. Sergeeva, A. N. and Pavlenko, L. I., *Zh. Neorg. Khim.* 12, 2063 (1967).
9. Williams, R. J., Cromer, D. T., and Larson, A. C., *Acta Crystallogr.* B28, 858 (1972).
10. Cromer, D. T. and Larson, A. C., *Acta Crystallogr.* 15, 397 (1962).
11. Williams, R. J., Cromer, D. T., and Larson, A. C., *Acta Crystallogr.* B27, 1701 (1971).
12. Cromer, D. T., *J. Phys. Chem.* 1957, 61.
13. Dunaj-Jurčo, M. and Boča, R., *Proc. IX Conf. Coord. Chem.*, p. 73. Smolenice—Bratislava, 1983.

Translated by J. Kožíšek and T. Guttmanová