Crystal and Molecular Structure of Bis(4-bromopyridine)dithiocyanate Copper(II)

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Abstract

The crystal structure of Cu(4-Brpy)$_2$(NCS)$_2$* exhibits two symmetrically independent pseudo-octahedral coordination polyhedra of Cu(II). The unit cell parameters are: $a = 8.568(3)$, $b = 9.200(3)$, $c = 10.809(5)$ Å, $\alpha = 72.64(3)$, $\beta = 86.15(3)$, $\gamma = 80.14(3)^\circ$, triclinic symmetry, space group $P1$, $Z = 2$. The crystal structure data are discussed and compared with those of Cu(4-pic)$_2$(NCS)$_2$ and Cu(py)$_2$(NCS)$_2$. As the comparison shows, changed properties of the neutral ligands in these complexes do not influence the coordination mode of the thiocyanate ligand, but they manifest themselves in the different strength of its coordination to the central atom as also in the degree of axial distortion of the Cu(II) coordination polyhedra.

Introduction

The donor–acceptor properties of neutral ligands are one of the factors influencing the coordination mode of thiocyanate ligands in heterogeneous thiocyanate complexes. It was Norbury [1] who generalized this finding for all transition metal complexes by his conception of the π-bonding hypothesis. In ref. 2, we showed that the validity of this hypothesis depends on the measure of manifestation of π-acceptor properties of neutral ligands, in conditions of the coordination spheres of different central atoms. Thiocyanato copper(II) complexes show an increased sensibility in this respect. This may be brought into connection with the plasticity of their coordination spheres [3].

As we have found, ligands of different π-acceptors properties in thiocyanato-copper(II) complexes can influence in several ways the bonding properties of thiocyanate ligands. They cause, for example, changes in the coordination mode [4], influence the electron transfer of thiocyanate ligand–central atom Cu(II) [5], effect the strength of its bonding to the central atom [6], as also its reactivity in thermal decomposition of thiocyanatocopper(II) complexes [7, 8].

The solution of the crystal structure of Cu(4-pic)$_2$(NCS)$_2$ [9] showed that the different properties of 4-picoline from those of pyridine in Cu(py)$_2$(NCS)$_2$ [10] are also manifested in a change of the degree of tetragonal distortion of the Cu(II) coordination polyhedron. Therefore the crystal structure of an analogical copper(II) complex was solved, which, however, exhibits on the pyridine ligands a substituent with a contrary directed induction effect.

Experimental

Preparation

Dark-green prism-shaped crystals of Cu(4-Brpy)$_2$ (NCS)$_2$ were prepared by reaction of an aqueous ammonia solution of CuSO$_4$ with an ethanol solution of 4-bromopyridine, an aqueous solution of 4-bromopyridine and an aqueous solution of NH$_4$NCS in the molar ratio of [Cu(II)] : [NH$_3$] : [4-Brpy] : [NCS$^-$] = 1:4:3:2.

Crystal Data

$CuBr_2S_2N_4C_{12}H_{10}$, $M_r = 495.70$, triclinic, $a = 8.568(3)$, $b = 9.200(3)$, $c = 10.809(5)$ Å, $\alpha = 72.64(3)$, $\beta = 86.15(3)$, $\gamma = 80.14(3)^\circ$, $U = 801.10(51)$ Å^3, $Z = 2$, $D_o = 2.109$ Mg m^{-3}, $D_c = 2.06$ Mg m^{-3}, $F(000) = 482$, μ(Cu Kα) = 10.8 mm^{-1}, space group $P1$.

A crystal of approximate dimensions 0.1 × 0.15 × 0.3 mm was selected for intensity and unit-cell measurements. Initially, unit cell parameters were determined from single crystal oscillation and Weissenberg photographs using Cu Kα radiation. Accurate cell parameters were obtained on a SYNTEX P2$_1$ diffractometer from a least-squares fit to 15 reflections. Intensity data with $\theta < 2\theta \leqslant 100^\circ$ were collected on a SYNTEX P2$_1$ diffractometer by

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*Abbreviations: py = pyridine, 4-pic = 4-picoline, 4-Brpy = 4-bromopyridine.

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the θ:2θ scanning technique, using graphite monochromated Cu Kα radiation (λ = 1.54178 Å). The scan rate was determined automatically within 4.88–29.3° min^{-1} in 2θ. Two standard reflections measured in an interval of 98 measured reflections showed no significant crystal deterioration. Of the 1651 independent reflections measured, 1274 had intensities greater than $I \geqslant 1.96\sigma(I)$ and these were used for the structure analysis. Lorentz, polarization, absorption and anomalous dispersion corrections were applied.

Structure Determination

The bromine position was obtained from the three dimensional Patterson map. Using the heavy-atom method, with bromine as the heavy atom, a few cycles of structure factors and Fourier calculations revealed 42 non-hydrogen atoms. Scattering factors for each type of atom were assigned in terms of their heights, and anisotropic thermal parameters, allocated in the later least-squares refinement, gave an R factor of 0.12. Inclusion of 16 hydrogen atoms in calculated positions, and a few more cycles of least-squares refinement, reduced R to 0.056.

The maximum of residual electron density in the final difference fourier synthesis was 0.60 e Å^{-3}. Neutral atom scattering factors were taken from the 'International Tables for X-ray Crystallography' [11]. The calculations were carried out partly on a NOVA 1200 computer using XTL program system [12] and partly on a MINSK M-4030-1 computer using NRC-program system [13]. Final atomic parameters are given in Table I. Bond lengths and bond angles are given in Table II. Least-squares planes data are given in Table III. An illustration of the two symmetrically independent molecules is given in Fig. 1, while their packing in the crystal structure is given in Fig. 2. See also 'Supplementary material'.

TABLE I. Final Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses, and B_{eq} for Non-hydrogen Atoms. $B_{eq} = (4/3)\Sigma_i\Sigma_jB_{ij}\bar{a}_i\bar{a}_j$.

Atom	x	y	z	B_{eq} (Å^2)
Br1	2059(3)	6139(3)	−816(3)	4.90
Br2	7340(3)	8190(4)	9827(3)	5.12
Br3	12742(3)	1327(4)	273(3)	5.62
Br4	6783(3)	2740(4)	1229(3)	5.46
Cu1	4744(11)	7139(9)	4562(9)	3.97
Cu2	9754(10)	2187(8)	4491(9)	3.76
S1	2835(7)	12487(7)	3226(6)	4.33
S2	6473(7)	1837(6)	5781(6)	4.32
S3	7955(7)	7530(7)	3186(6)	3.90
S4	11456(7)	−3155(6)	5840(6)	3.53
N1	4020(20)	9356(18)	3794(19)	4.31
N2	5368(21)	4927(21)	5230(20)	5.00
N3	9248(17)	4370(17)	4163(14)	2.01
N4	9941(31)	−150(22)	4985(28)	8.30
N11	3805(22)	6816(21)	2945(17)	4.17
N21	5518(19)	7556(20)	6120(16)	3.54
N31	10659(20)	1912(19)	6255(18)	4.15
N41	8800(19)	2336(20)	2762(15)	3.55
C1	3563(21)	10626(24)	3558(17)	2.95
C2	5844(24)	3652(24)	5478(21)	4.01
C3	8802(25)	5570(25)	3829(20)	3.59
C4	10597(24)	−1307(23)	5374(18)	3.43
C11	4820(22)	5886(23)	2184(21)	3.48
C12	4350(24)	5704(23)	1156(20)	3.37
C13	2714(27)	6348(26)	751(21)	4.50
C14	1771(28)	7096(29)	1472(25)	5.33
C15	2384(25)	7310(31)	2488(26)	5.48
C21	4693(25)	8340(27)	6656(23)	4.43
C22	5142(26)	8613(27)	7904(24)	4.74
C23	6541(28)	8037(25)	8281(22)	4.14
C24	7588(21)	7067(27)	7635(19)	3.51
C25	7013(27)	6939(26)	6465(21)	4.26
C31	10108(37)	707(38)	7269(25)	7.76
C32	10922(26)	698(25)	8609(20)	4.09
C33	11995(31)	1443(26)	8696(23)	5.05
C34	12394(28)	2804(29)	7548(22)	4.94
C35	11633(27)	2879(26)	6428(18)	4.05
C41	7723(25)	1418(26)	2781(27)	5.14
C42	7127(27)	1611(23)	1524(23)	4.17
C43	7521(22)	2508(21)	434(20)	2.80
C44	8701(26)	3593(27)	501(23)	4.76
C45	9162(22)	3382(21)	1651(20)	2.98
H11	6013	5436	2685	
H12	5150	5079	782	
H14	734	7490	1211	
H15	1755	8028	2966	
H21	3631	8917	6528	
H22	4498	9094	8625	
H24	8767	6522	7981	
H25	7860	6338	5933	
H31	9621	91	7188	
H32	10386	−10	9309	
H34	13173	3498	7541	
H35	11809	3915	5459	
H41	7264	820	3437	
H42	6334	914	1407	
H44	8962	4441	9539	
H45	10831	4075	1817	

Discussion

The unit cell of the crystal structure of Cu(4-Brpy)$_2$(NCS)$_2$ contains two symmetrically independent coordination polyhedra Cu(II). The central atom has a pseudooctahedral coordination with the same ligand arrangement in both coordination spheres. There are in the equatorial planes in the *trans*-position two thiocyanate and two 4-bromopyridine ligands coordinated. Two sulphur atoms from

TABLE II. Bond Lengths (Å) and Angles (°) in the Complex

Intermolecular distances

Cu1–N1	1.958(8)	Cu2–N3	1.919(20)
Cu1–N2	1.949(20)	Cu2–N4	2.038(20)
Cu1–N11	2.085(20)	Cu2–N31	2.036(20)
Cu1–N21	2.003(20)	Cu2–N41	2.036(20)
Cu1–S4*	3.078(10)	Cu2–S2	3.070(10)
Cu1–S3	3.058(10)	Cu2–S1*	2.911(10)
N1–C1	1.127(20)	N3–C3	1.085(26)
C1–S1	1.663(22)	C3–S3	1.743(22)
N2–C2	1.120(26)	N4–C4	1.077(27)
C2–S2	1.601(20)	C4–S4	1.661(20)
N21–C25	1.333(27)	N31–C35	1.386(27)
N21–C21	1.183(27)	N31–C31	1.402(30)
C21–C22	1.546(31)	C31–C32	1.616(32)
C22–C23	1.271(30)	C32–C33	1.275(33)
C23–C24	1.440(30)	C33–C34	1.505(32)
C23–Br2	1.896(20)	C33–Br3	1.840(22)
C24–C25	1.440(30)	C34–C35	1.392(29)
N11–C11	1.498(27)	N41–C41	1.331(27)
N11–C15	1.308(26)	N41–C45	1.359(26)
C11–C12	1.284(27)	C41–C42	1.451(32)
C12–C13	1.461(28)	C42–C43	1.293(28)
C13–C14	1.344(20)	C43–C44	1.522(28)
C13–Br1	1.882(19)	C43–Br4	1.880(19)
C14–C15	1.365(22)	C44–C45	1.293(29)

Intramolecular distances

Br1–S4	3.534(10)	Br2–Br4**	3.948(7)
Br1–Br3	4.174(8)	Br3–S1	3.665(10)
Br1–Br4*	4.756(8)	Br3–Br4*	3.980(8)
Br2–S3*	3.558(10)	Br4–S2*	3.605(10)
Br2–Br3*	4.557(8)		

N1–Cu1–N2	175.7(7)	N3–Cu2–N4	171.3(9)
N11–Cu1–N21	176.1(8)	N32–Cu2–N41	176.8(8)
S4*–Cu1–S3	177.8(4)	S2–Cu2–S1*	178.6(4)
N2–Cu1–N21	93.8(8)	N4–Cu2–N31	86.7(8)
N2–Cu1–N11	88.9(8)	N4–Cu2–N41	90.3(8)

TABLE II. *(continued)*

N1–Cu1–N11	87.0(6)	N4–Cu2–S2	81.0(8)
N1–Cu1–N21	90.2(6)	N4–Cu2–S1	98.4(8)
S4*–Cu1–N1	89.8(6)	N3–Cu2–N31	91.7(7)
S4*–Cu1–N2	90.6(7)	N3–Cu2–N41	91.1(7)
S4*–Cu1–N11	87.2(6)	N3–Cu2–S2	89.7(6)
S4*–Cu1–N21	91.6(6)	N3–Cu2–S1*	90.9(6)
S3–Cu1–N1	88.4(6)	N31–Cu2–S1*	91.8(6)
S3–Cu1–N2	91.1(7)	N31–Cu2–S2	89.4(6)
S3–Cu1–N11	91.4(6)	N41–Cu2–S1*	90.0(6)
S3–Cu1–N21	89.7(6)	N41–Cu2–S2	88.7(6)
Cu1–N1–C1	169(1)	Cu2–N3–C3	167(2)
N1–C1–S1	178(1)	N3–C3–S3	175(2)
Cu1–N2–C2	171(2)	Cu2–N4–C4	154(2)
N2–C2–S2	177(2)	N4–C4–S4	174(2)
Cu1–N21–C21	120(1)	Cu2–N31–C31	115(1)
Cu1–N21–C25	116(1)	Cu2–N31–C35	122(1)
C21–N21–C25	123(2)	C31–N31–C35	123(2)
Br2–C23–C22	122(2)	Br3–C33–C32	120(2)
Br2–C23–C24	116(2)	Br3–C33–C34	116(2)
C22–C23–C24	122(2)	C32–C33–C34	122(2)
N21–C21–C22	123(2)	N31–C31–C32	109(2)
C21–C22–C23	115(2)	C31–C32–C33	124(2)
C23–C24–C25	117(2)	C33–C34–C35	112(2)
C24–C25–N21	119(2)	C34–C35–N31	127(2)
Cu1–N11–C15	128(1)	Cu2–N41–C41	118(1)
Cu1–N11–C11	119(1)	Cu2–N41–C45	122(1)
C11–N11–C15	113(2)	C41–N41–C45	120(2)
Br1–C13–C14	121(1)	Br4–C43–C42	127(2)
Br1–C13–C12	119(1)	Br4–C43–C44	117(1)
C12–C13–C14	120(2)	C42–C43–C44	116(2)
N11–C11–C12	123(2)	N41–C41–C42	114(2)
C11–C12–C13	119(2)	C41–C42–C43	127(2)
C13–C14–C15	117(1)	C43–C44–C45	114(2)
C14–C15–N11	128(2)	C44–C45–N41	129(2)

S1* at $x + 1, y - 1, z$; S2* at $x, y - 1, z$: S3* at $x, y, z + 1$; S4* at $x - 1, y + 1, z$; Br3* at $x - 1, y + 1, z$; Br4* at $x + 1, y, z$; Br4** at $x, y + 1, z$.

TABLE III. Least-squares Planes Data

Plane	Atoms defining plane	l	m	n	p
(a) Least-squares planes and their equations given by $lX + mY + nZ - p = 0$, where X, Y and Z are orthogonal coordinates (Å), l, m and n are the direction cosines of the normal to the plane and p is the distance of the plane from the origin					
1	N1, N2, N11, N12	0.8845	−0.0526	0.4336	2.2535
2	N11, C11–C15	0.4195	0.7094	−0.5663	5.2135
3	N21, C21–C25	0.4635	0.6912	−0.5545	5.5414
4	N4, N3, N31, N41	−0.3334	0.6767	−0.7458	3.1226
5	N41, C41–C45	0.6275	−0.7665	−0.1370	2.3782
6	N31, C31–C35	0.6549	−0.7334	−0.1823	3.0442

Plane	Deviations
(b) Deviations (Å) of relevant atoms from least-squares planes defined above	
1	N1, 0.013; N2, 0.012; N11, −0.012; N12, −0.012; Cu1, 0.036
2	N11, 0.015; C11, −0.032; C12, 0.014; C13, 0.019; C14, −0.034; C15, 0.016
3	N21, −0.024; C21, 0.014; C22, −0.017; C23, 0.029; C24, −0.034; C25, 0.033

(continued)

TABLE III. *(continued)*

4	N4, −0.009; N3, −0.009; N31, 0.010; N41, 0.009; Cu2, −1.383
5	N41, 0.030; C41, −0.009; C42, −0.016; C43, 0.020; C44, 0.000; C45, −0.025
6	N31, 0.017; C31, 0.012; C32, −0.020; C33, 0.016; C34, 0.016; C35, −0.041

Planes	Angle	Planes	Angle	Planes	Angle
1−2	53.4	2−3	2.8	3−5	48.9
1−3	50.9	2−4	46.3	3−6	95.9
1−4	88.8	2−5	101.7	4−5	123.3
1−5	48.8	2−6	98.2	4−6	120.4
1−6	45.4	3−4	48.9	5−6	3.6

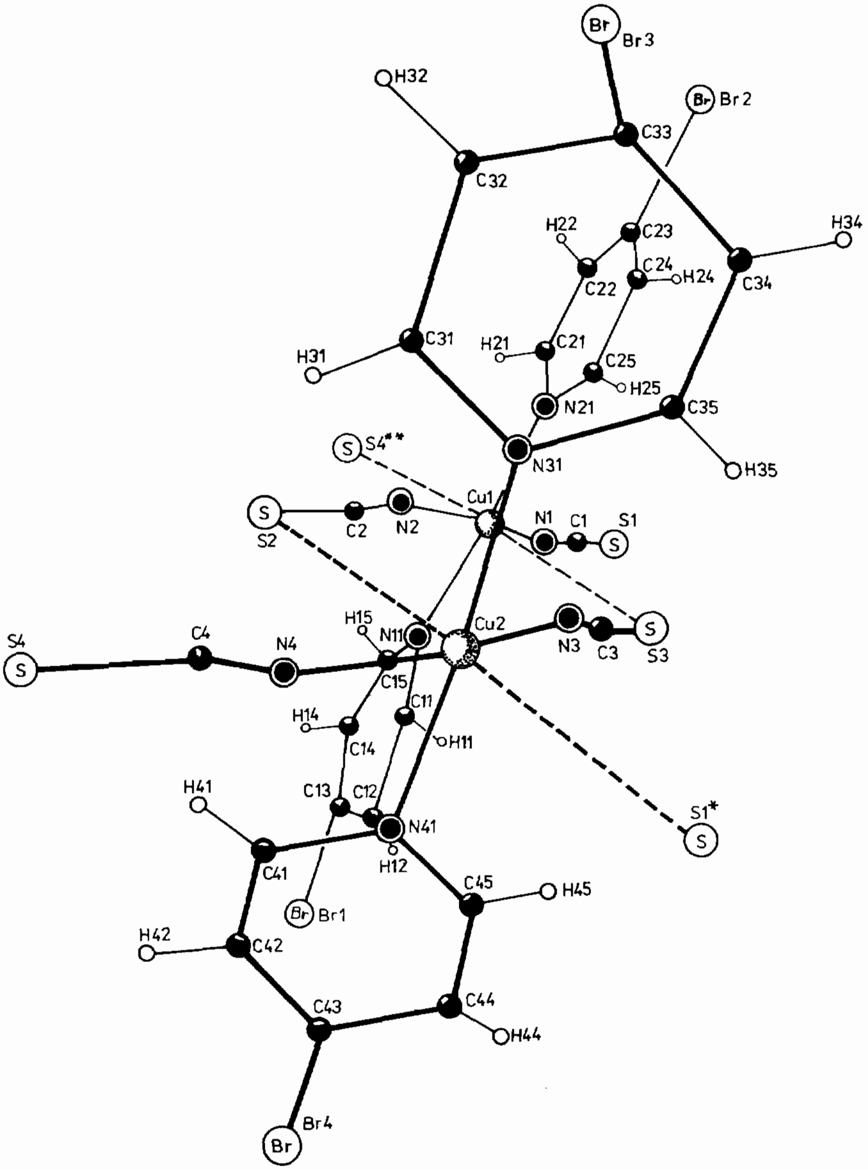

Fig. 1. A view of the $Cu(4\text{-}Brpy)_2(NCS)_2$ molecular structure, showing the atom numbering.

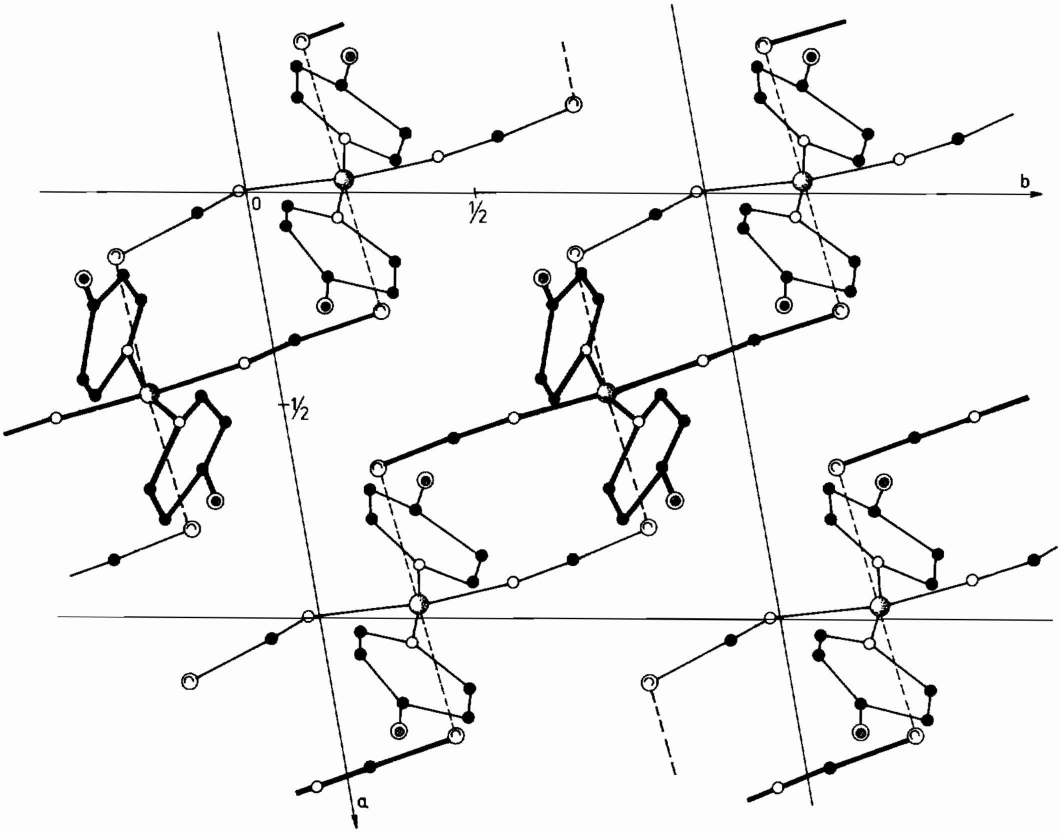

Fig. 2. The orthogonal projection of the crystal structure $Cu(4\text{-}Brpy)_2(NCS)_2$ to the *a*, *b* plane.

TABLE IV. Bond Distances of $CuL_2(NCS)_2$ Complexes (Å)

L	Pyridine [10]	4-Bromopyridine	4-Picoline [9]
Cu1–N(NCS)	1.94(2)	1.96(1) 1.95(2)	1.95(1) 1.93(1)
Cu2–N(NCS)		1.92(2) 2.04(2)	1.92(1) 1.94(1)
Cu3–N(NCS)			1.95(1) 1.97(1)
Cu1–N(L)	1.98(2)	2.09(2) 2.00(2)	2.05(1) 2.00(1)
Cu2–N(L)		2.04(2) 2.04(2)	2.07(1) 2.07(1)
Cu3–N(L)			2.02(1) 2.03(1)
Cu1–S	3.04(3)	3.06(1) 3.08(1)	3.11(0) 3.11(0)
Cu2–S		3.07(1) 2.91(1)	2.98(0) 2.99(0)
Cu3–S			2.98(0) 3.26(0)

the bridging bidentate thiocyanate ligands are coordinated to the central atom in the axial position. The found coordination mode of Cu(II) is analogous to that in the crystal structure of $Cu(py)_2(NCS)_2$ [10] and $Cu(4\text{-}pic)_2(NCS)_2$ [9].

Both types of Cu(II) coordination polyhedra alternate in the chain and they are linked together by thiocyanate ligands. The distances between bromine and sulphur atoms in the frame of the chain can be considered as van der Waals interactions. Other distances between atoms of neighbouring chains are greater than a sum of their van der Waals radii. The analysis of the intrachain distances shows that the placement of both symmetrically independent coordination polyhedra in the crystal structure is equivalent.

The two coordination polyhedra found in $Cu(4\text{-}Brpy)_2(NCS)_2$ differ from each other by the degree of their axial distortion. This conslusion is evidenced from the values of interatomic distances as listed in Table IV. Bond lengths in the coordination polyhedra in the crystal structures of $Cu(py)_2$-

TABLE V. Infrared and Electronic Spectral Data of $CuL_2(NCS)_2$ Complexes (cm^{-1})

L	d–d	*CT*	$\nu(Cu-N_L)$	$\nu(Cu-N_{NCS})$	$\nu(CN)$
Pyridine [5, 6]	15600	24000	257s	321s	2072s
4-Picoline [5, 6]	13400sh, 16200	24700	262s	363w 321s	2100sh, 2080s
4-Bromopyridine [14]	16000	23700	237s, 248s	336s	2097s

$(NCS)_2$ and $Cu(4\text{-pic})_2(NCS)_2$ complexes are also given.

The values of the distances Cu–N(NCS), except that of 2.04(2) Å, in the compared coordination polyhedra are similar and are in the interval of 1.92(2)–1.97(1) Å. The values of the compared distances of Cu–N(L) are within the interval of 1.92(2)–2.09(2) and are also analogous to each other. The average value of the observed interatomic distances of Cu–N(L) compared with the average value of the studied interatomic distances Cu–N(NCS) is greater by 0.1 Å. This result shows good agreement with the values of valence vibration of Cu–N(NCS) and Cu–N(L) read from the infrared spectra (see Table V).

The differences in the axial distortions of the coordination polyhedra under discussion are connected with the different values of the interatomic distances of Cu–S. The crystal structure of $Cu(py)_2(NCS)_2$ contains only one type of coordination polyhedron with two Cu–S bonds of the same length. The exchange of the pyridine ligands by their 4-methyl derivatives in the coordination polyhedron causes the crystal structure of $Cu(4\text{-pic})_2NCS_2$ to exhibit three symmetrically independent coordination polyhedra of Cu(II). The axial distortion in the first of them is greater as in the pyridine complex and presents itself by elongation of both the Cu–S bonds by the average value of ≈0.07 Å. In the second coordination polyhedron a shortening of both the Cu–S bonds was found with an average value of ≈0.05 Å. The change of the axial distortion in the third polyhedron of Cu(II) is unsymmetrical; one of the Cu–S bonds shows a shortening by 0.06 Å, while the other appears expressively elongated by 0.22 Å.

The exchange of the pyridine ligand by its 4-bromine derivatives in the complex had the consequence that in the crystal structure of $Cu(4\text{-Brpy})_2(NCS)_2$ there are two symmetrically independent coordination polyhedra of Cu(II). The axial distortion in the first polyhedron is moderately increased, both Cu–S bonds being elongated by the average value of ≈0.03 Å. The axial distortion in the other Cu(II) polyhedron has unsymmetrically changed, one of the Cu–S bonds has become elongated by ≈0.03 Å, whereas the other shows an expressive shortening by 0.13 Å.

In the thiocyanato copper(II) complexes studied the presence of ligands of the type of pyridine, 4-picoline and 4-bromopyridine with respect to their different p*K* values, differently influences the potential ability of the central atom to undergo processes. For example, in agreement with the higher basicity of 4-picoline compared with pyridine, the $Cu(4\text{-pic})_2\cdot(NCS)_2$ showed the maximum of CT band shifted to higher energies, and on the contrary, the lowered value of basicity of 4-bromopyridine against pyridine causes in the respective complex the maximum of the CT band to be shifted in the contrary direction [14](see Table V).

The thiocyanate ligand applies its reducing properties especially in its coordination by sulphur and such a coordination mode is realized only in the axial position of Cu(II) coordination polyhedra [4]. Based on this knowledge it is possible just in the observed changes of interatomic distances Cu–S to search for mutual conditionality between the properties of the neutral ligand L and the redox properties of the central atom in the respective thiocyanate complex.

In one of the couples of coordination polyhedra in $Cu(4\text{-Brpy})_2(NCS)_2$ complex a significant shift of the Cu(II) atom out of the equatorial plane was observed. In agreement with the conception of a lowered redox stability of complex $Cu(4\text{-Brpy})_2(NCS)_2$ we take such changes in coordination polyhedra as an intermediate stage of transition of the pseudooctahedral coordination to the tetrahedral form, typical of Cu(I).

Supplementary Material

Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the Editor-in-Chief.

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