

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS(THIO-CYANATO)-BIS(4-METHYLPYRIDINE)COPPER(II) COMPLEX AT 180°K

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At 180°K, $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ crystallizes in the monoclinic system, space group $P2_1$, $Z = 6$, with the elementary cell parameters $a = 0.963(1)$, $b = 2.653(2)$, $c = 0.984(2)$ nm, $\beta = 106.40(0.07)^\circ$. The central atom possesses the tetragonal bipyramidal coordination; the heterocyclic ligands are bonded in the equatorial plane of the coordination polyhedron in the *trans* positions, the thiocyanate ligands are bridge ones and are coordinated in both the equatorial and axial positions of the coordination polyhedron. The crystal structure involves three symmetrically independent coordination polyhedra differing in the degree of axial distortion. The thermal stability of the thiocyanate ligands in the complex is related with the steric arrangement of the thiocyanatocopper(II) chains.

During the study of the thermal properties of $[\text{CuL}_2(\text{NCS})_2]$ complexes where L is pyridine or the various isomeric forms of methylpyridine or dimethylpyridine^{1,2}, methyl substituents at the pyridine ligand were found to affect the starting temperature of redox transformations of the thiocyanate ligand. For the $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ complex the temperature at which the thiocyanate ligands start to decompose is appreciably lower than for the $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ complex³. This is rather surprising because owing to the higher basicity and a positive inductive effect, 4-methylpyridine in thiocyanatocopper(II) complexes should increase their redox stability as compared to pyridine. The elucidation of the crystal structure of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$, which is the objective of the present work, should contribute to gaining insight into this effect.

EXPERIMENTAL

The substance studied was obtained by reacting 10 ml of an aqueous solution of CuSO_4 (2 mol \cdot l^{-1}) containing ammonia with an ethanolic solution of 4-methylpyridine (1 : 1) and an aqueous solution of NH_4NCS (2 mol l^{-1}), added in amounts such that the $c(\text{Cu}) : c(\text{NH}_3) : c(4\text{-Mepy}) : c(\text{NCS})$ ratio was 2 : 8 : 5 : 4. The green needle-shaped crystals were filtered out and rinsed with 1% aqueous and 1% ethanolic solutions of 4-methylpyridine. For $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2(\text{NCS})_2$ (365.96)

calculated: 45.96% C, 3.86% H, 17.37% Cu, 15.31% N; found: 45.94% C, 3.82% H, 17.37% Cu, 15.30% N.

Crude crystallographic data were obtained by using the oscillation Weissenberg photographic method. The specific weight of the crystals was determined by means of the flotation method in a bromoform-methanol mixture. The experimental data were obtained on a SYNTEX P2₁ automatic diffractometer at 180 K. The lattice parameters were derived by refinement of the position angles of ten selected diffractions on a Polaroid photograph from the diffractometer. Conditions of measurement were as follows: CuK α radiation (1.54178), graphite monochromator, $\theta - 2\theta$ scanning technique at rates of 4.83–29.3° min⁻¹, crystal dimensions 0.1 × 0.1 × 0.5 mm, temperature 180 K, checking by intensity measurements of two diffractions after each 98 diffractions, conditions for observed diffractions: $I = 3\sigma(I)$, number of observed diffractions 2374. Intensity fluctuations of the standard diffractions did not exceed 1%. The experimental diffraction intensities were corrected for the Lorentz polarization factor and absorption by measuring the Ψ scan of selected diffractions.

The crystal structure was elucidated by using the heavy atom method. The positions of the copper atoms were determined by Patterson synthesis and those of the remaining nonhydrogen atoms, by Fourier synthesis. The positions of the hydrogen atoms were calculated assuming the sp^2 and sp^3 hybridization. The least squares method was employed for the structure refinement. In the isotropic refinement, all parameters were refined with a full matrix, whereas in the anisotropic refinement, the parameters were divided into nine groups and refined with a block-diagonal matrix. The final values of $R = 0.063$ and weighted $R_w = 0.063$ ($w = 1/\sigma^2(F)$) were achieved. The scattering curves of the neutral atoms were taken from the International Tables⁴. The calculations were performed on a NOVA 1200 computer using the XTL programs⁵ and on a MINSK-M-4030-1 computer using the programs SHELX (ref.⁶) and PARST (ref.⁷).

RESULTS AND DISCUSSION

The [Cu(4-Mepy)₂(NCS)₂] complex crystallizes in the monoclinic system, space group $P2_1$, $Z = 6$, with elementary cell parameters as given in Table I. The fractional coordinates of the nonhydrogen atoms are given in Table II, the bond lengths (internuclear distances) and angles, in Tables III and IV, respectively; some interatomic distances for this substance and for [Cu(py)₂(NCS)₂] at room temperature are also included. The values of the observed and calculated structure factors, anisotropic temperature factors, fractional coordinates of the hydrogen atoms and their bond distances and equations for the planes formed by the nitrogen atoms in the equatorial planes of the coordination polyhedra and the pyridine ring atoms as well as the angles formed by them are available from the authors on request.

In the crystal structure of [Cu(4-Mepy)₂(NCS)₂] the central atom possesses the tetragonally bipyramidal coordination and CuN₄S₂ chromophors. Similarly as in [Cu(py)₂(NCS)₂] (ref.⁸), the thiocyanate and heterocyclic ligands are coordinated by the nitrogen atoms in the equatorial plane of the coordination polyhedron of Cu(II). In the axial positions the central atom is coordinated by sulphur atoms from the bridge thiocyanate ligands. In the crystal structure of [Cu(4-Mepy)₂(NCS)₂], in contrast to [Cu(py)₂(NCS)₂], three symmetrically independent coordination polyhedra, with different degrees of axial distortion, occur about the copper atoms (Fig. 1).

TABLE I
Crystallographic data of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]^a$

Crystallographic system	monoclinic
Space group	$P2_1, Z = 6$
Elementary cell dimensions	
<i>a</i> , nm	0.963(1)
<i>b</i> , nm	2.653(2)
<i>c</i> , nm	0.984(2)
β , deg	106.40(7)
<i>V</i> , nm ³	2.413(3)
Density at room temperature, 10^3 kg m^{-3}	$d_o = 1.48(1), d_c = 1.47$
$\mu(\text{CuK}\alpha)$, mm^{-1}	42.4
<i>F</i> (000)	1 122

^a Diffraction region measured: *h*: -9 to 9, *k*: 0 to 26, *l*: 0 to 9; 2θ diffraction angle region for lattice parameter refinement: 9.94° to 23.12° ; final differential map: $\Delta\rho_{\text{max}}: 1.35 \cdot 10^3 \text{ e nm}^{-3}$, $\Delta\rho_{\text{min}}: -1.86 \cdot 10^3 \text{ e nm}^{-3}$, $(\Delta/\sigma)_{\text{max}}: 0.30$.

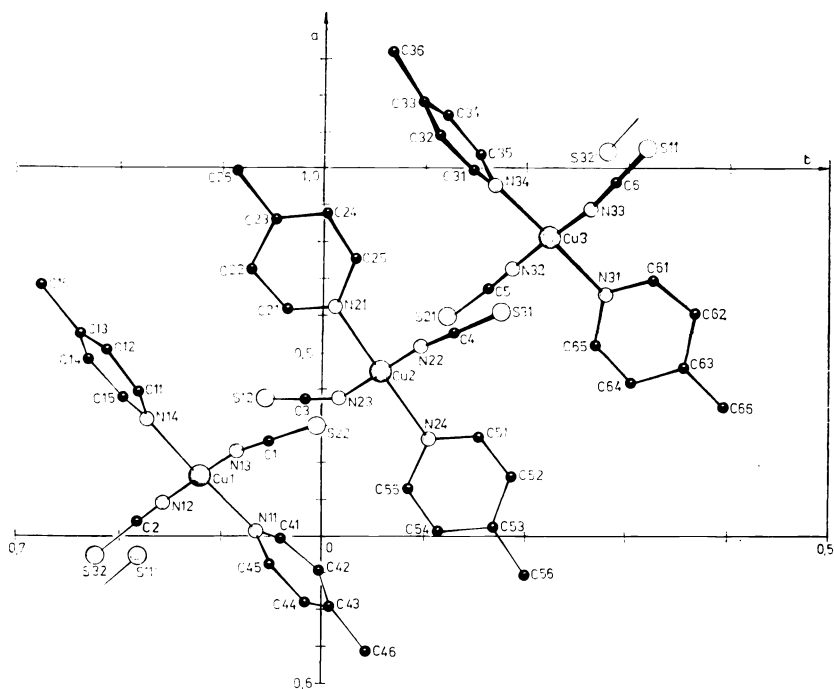


FIG. 1
Orthogonal projection of the crystal structure of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ into the *xy* plane

TABLE II

Fractional coordinates of atoms and their temperature factors $B_{\text{eq}} = (8/3\pi^2) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ for the nonhydrogen atoms. The standard deviations are given in parentheses

Atom	(x/a) · 10 ⁴	(y/b) · 10 ⁴	(z/c) · 10 ⁴	$B_{\text{eq}} \cdot 10^{-4}$ nm ²
Cu(1)	1629(0)	-1221(0)	210(0)	164(7)
N(12)	910(16)	-1547(6)	-1553(15)	231(46)
C(2)	304(19)	-1815(7)	-2488(18)	164(53)
S(32)	-475(5)	-2210(2)	-3819(4)	204(12)
S(32')	10475(5)	2790(2)	38198(4)	204(12)
N(13)	2320(15)	-857(6)	1998(14)	192(43)
C(1)	2619(18)	-519(7)	2855(17)	153(51)
S(22)	3001(5)	-71(2)	3969(4)	181(12)
Cu(2)	4450(2)	574(1)	2326(2)	145(7)
N(22)	5119(17)	992(6)	3997(15)	219(50)
C(4)	5526(18)	1296(6)	4903(17)	143(47)
S(31)	6066(5)	1705(2)	6140(4)	175(13)
N(23)	3745(15)	171(6)	637(15)	194(34)
C(3)	3751(16)	-173(7)	-98(17)	128(50)
S(12)	3765(5)	-663(2)	-1124(4)	203(13)
Cu(3)	8044(3)	2215(1)	4813(2)	148(7)
N(32)	7280(15)	1867(6)	3070(15)	211(45)
C(5)	6738(17)	1602(7)	2097(18)	116(46)
S(21)	5979(5)	1202(2)	792(4)	199(12)
N(33)	8937(16)	2585(6)	6564(15)	189(44)
C(6)	9577(19)	2839(8)	7437(18)	189(48)
S(11')	-548(5)	-1808(2)	1236(4)	193(13)
S(11)	10548(5)	3192(2)	8764(4)	193(13)
N(14)	3242(13)	-1712(5)	838(13)	131(39)
C(11)	3 943(19)	-1 810(7)	2 258(16)	219(54)
C(12)	5 036(19)	-2140(7)	2703(16)	225(57)
C(13)	5574(17)	-2401(6)	1735(16)	153(49)
C(14)	4 865(24)	-2308(8)	220(22)	362(71)
C(15)	3806(19)	-1973(7)	-53(17)	238(53)
C(16)	6837(20)	-2780(8)	2209(21)	328(61)
N(11)	144(14)	-671(5)	-465(13)	140(41)
C(41)	-54(18)	-414(6)	-1716(16)	199(48)
C(42)	-975(21)	-53(7)	-2169(17)	233(59)
C(43)	-1953(21)	80(6)	-1457(17)	178(52)
C(44)	-1825(18)	-170(6)	-136(18)	201(54)
C(45)	-769(19)	-529(7)	338(17)	170(56)
C(46)	-3166(22)	445(7)	-2055(18)	358(64)
N(21)	6 240(14)	119(5)	2998(13)	117(41)
C(21)	6 123(19)	-377(7)	2868(17)	229(58)

TABLE II
(Continued)

Atom	$(x/a) \cdot 10^4$	$(y/b) \cdot 10^4$	$(z/c) \cdot 10^4$	$B_{\text{eq}} \cdot 10^{-4}$ nm ²
C(22)	7278(19)	-706(7)	3361(17)	198(53)
C(23)	8661(18)	-492(7)	3 968(16)	166(56)
C(24)	8787(18)	16(7)	4029(16)	161(50)
C(25)	7561(19)	323(7)	3555(16)	236(57)
C(26)	9940(19)	-853(7)	4570(18)	248(56)
N(24)	2661(14)	1030(5)	1653(13)	135(41)
C(51)	2777(19)	1529(7)	1587(18)	188(56)
C(52)	1630(18)	1854(7)	1092(18)	239(50)
C(53)	221(19)	1662(6)	649(16)	156(54)
C(54)	114(17)	132(7)	762(16)	169(49)
C(55)	1284(19)	839(6)	1220(16)	171(54)
C(56)	-1041(20)	2006(6)	180(17)	222(41)
N(34)	9542(14)	1684(5)	5428(13)	122(41)
C(31)	9875(17)	1485(6)	6794(16)	189(49)
C(32)	10996(17)	1151(6)	7286(16)	154(46)
C(33)	11865(19)	996(6)	6450(16)	192(48)
C(34)	11497(20)	1214(7)	5075(17)	233(53)
C(35)	10360(17)	1526(6)	4608(15)	133(44)
C(36)	13154(21)	671(8)	7028(19)	337(60)
N(31)	6610(13)	2783(5)	4157(12)	100(42)
C(61)	6994(19)	3267(6)	4350(16)	166(50)
C(62)	6035(19)	3676(7)	3995(16)	220(59)
C(63)	4563(19)	3560(7)	3463(17)	206(54)
C(64)	4163(19)	3047(7)	3244(16)	219(52)
C(65)	5193(20)	2683(7)	3583(17)	226(55)
C(66)	3483(21)	3978(9)	3102(18)	352(66)

The Cu—N bond lengths in the symmetrically independent coordination polyhedra are not significantly different; they fall within the regions of 0.189–0.196 nm for Cu—N(NCS) and 0.198–0.205 nm for Cu—N(L). The Cu—S bond lengths, on the other hand, differ appreciably (Table III): while in the coordination polyhedron about Cu(2) the Cu—S bond lengths are comparable to those in [Cu(py)₂.(NCS)₂], they are significantly longer in the coordination polyhedron about Cu(1). In the coordination polyhedron about Cu(3), considerable asymmetry is observed in the bond lengths: one of the Cu—S bond lengths lies within the range for the

TABLE III
Internuclear distances in $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ at 180 K

Atoms	Distance nm	Atoms	Distance nm	Atoms	Distance nm
Cu(1)-N(11)	0·202(1) 0·202(1) ^a	Cu(3)-N(34)	0·198(1) 0·196(1) ^a	C(41)-C(42)	0·129(2)
Cu(1)-N(12)	0·189(1) 0·189(1) ^a	Cu(3)-S(32')	0·317(1) 0·326(1) ^a	C(42)-C(43)	0·137(3)
Cu(1)-N(13)	0·195(1) 0·196(1) ^a	Cu(3)-S(31)	0·293(1) 0·298(1) ^a	C(43)-C(44)	0·143(2)
Cu(1)-N(14)	0·199(1) 0·196(1) ^a	N(12)-C(2)	0·118(2)	C(44)-C(45)	0·138(2)
Cu(1)-S(12)	0·311(1) 0·311(1) ^a	C(2)-S(32)	0·168(2)	C(43)-C(46)	0·150(3)
Cu(1)-S(11')	0·301(1) 0·311(1) ^a	N(13)-C(1)	0·121(2)	N(21)-C(21)	0·123(2)
Cu(2)-N(21)	0·205(1) 0·208(1) ^a	C(1)-S(22)	0·159(2)	N(21)-C(25)	0·134(2)
Cu(2)-N(22)	0·194(2) 0·192(1) ^a	N(22)-C(4)	0·118(2)	C(21)-C(22)	0·139(2)
Cu(2)-N(23) ^b	0·193(1) 0·193(1) ^a	C(4)-S(31)	0·160(2)	C(22)-C(23)	0·142(2)
Cu(2)-N(24) ^c	0·205(1) 0·205(1) ^a	N(23)-C(3)	0·117(2)	C(23)-C(24)	0·135(3)
Cu(2)-S(21)	0·292(1) 0·298(1) ^a	C(3)-S(12)	0·165(2)	C(24)-C(25)	0·140(2)
Cu(2)-S(22) ^d	0·296(1) 0·298(1) ^a	N(32)-C(5)	0·118(2)	C(23)-C(26)	0·154(2)
Cu(3)-N(31)	0·202(1) 0·204(1) ^a	C(5)-S(21)	0·167(2)	N(24)-C(51)	0·133(2)
Cu(3)-N(32)	0·190(1) 0·193(1) ^a	N(33)-C(6)	0·113(2)	N(24)-C(55)	0·137(2)
Cu(3)-N(33)	0·196(1) 0·193(1) ^a	C(6)-S(11)	0·166(2)	C(51)-C(52)	0·138(2)
		N(14)-C(11)	0·139(2)	C(52)-C(53)	0·140(2)
		N(14)-C(15)	0·135(2)	C(53)-C(54)	0·142(2)
		C(11)-C(12)	0·134(2)	C(54)-C(55)	0·134(2)
		C(12)-C(13)	0·139(2)	C(53)-C(56)	0·149(2)
		C(13)-C(14)	0·148(2)	N(34)-C(31)	0·140(2)
		C(14)-C(15)	0·132(2)	N(34)-C(35)	0·134(2)
		C(13)-C(16)	0·154(3)	C(31)-C(32)	0·137(2)
		N(11)-C(41)	0·138(2)	C(32)-C(33)	0·139(2)
		N(11)-C(45)	0·139(2)	C(33)-C(34)	0·142(2)
				C(34)-C(35)	0·134(2)
				C(33)-C(36)	0·148(3)
				N(31)-C(61)	0·133(2)

^a At 293 K, ref. ⁹; in $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ at 293 K (ref. ⁸); ^b 0·194(2); ^c 0·198(2); ^d 0·304(3) nm.

TABLE IV
Bond angles in $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ at 180 K

Atoms	Angle deg	Atoms	Angle deg
N(11)–Cu(1)–N(14)	174·0(7)	C(24)–C(25)–N(21)	121(2)
N(12)–Cu(1)–N(13)	177·4(7)	C(25)–N(21)–C(21)	119(2)
S(12)–Cu(1)–N(12)	86·8(5)	N(34)–C(31)–C(32)	122(2)
N(12)–C(2)–S(32)	177(2)	C(31)–C(32)–C(33)	122(2)
N(13)–C(1)–S(22)	179(2)	C(32)–C(33)–C(34)	114(2)
N(21)–Cu(2)–N(24)	179·9(6)	C(33)–C(34)–C(35)	122(2)
N(22)–Cu(2)–N(23)	178·5(8)	C(34)–C(35)–N(34)	123(1)
S(21)–Cu(2)–S(22)	177·8(1)	C(35)–N(34)–C(31)	117(1)
N(23)–C(3)–S(12)	179(2)	N(11)–C(41)–C(42)	126(2)
N(22)–C(4)–S(31)	179(2)	C(41)–C(42)–C(43)	121(2)
N(31)–Cu(3)–N(33)	176·5(7)	C(42)–C(43)–C(44)	117(2)
N(32)–Cu(3)–N(34)	176·3(8)	C(43)–C(44)–C(45)	120(2)
S(31)–Cu(3)–S(32')	171·9(1)	C(44)–C(45)–N(11)	121(2)
N(32)–C(5)–S(21)	177(2)	C(45)–N(11)–C(41)	115(1)
N(33)–C(6)–S(11)	178(2)	N(24)–C(51)–C(52)	125(2)
N(14)–C(11)–C(12)	124(2)	C(51)–C(52)–C(53)	119(2)
C(11)–C(12)–C(13)	121(2)	C(52)–C(53)–C(54)	115(2)
C(12)–C(13)–C(14)	117(2)	C(53)–C(54)–C(55)	122(2)
C(13)–C(14)–C(15)	115(2)	C(54)–C(55)–N(24)	123(2)
C(14)–C(15)–N(14)	130(2)	C(55)–N(24)–C(51)	116(2)
C(15)–N(14)–C(11)	113(1)	N(31)–C(61)–C(62)	125(2)
N(21)–C(21)–C(22)	124(2)	C(61)–C(62)–C(63)	117(2)
C(21)–C(22)–C(23)	117(2)	C(62)–C(63)–C(64)	118(2)
C(22)–C(23)–C(24)	119(2)	C(63)–C(64)–C(65)	120(2)
C(23)–C(24)–C(25)	120(2)	C(64)–C(65)–N(31)	123(2)
		C(65)–N(31)–C(61)	117(2)

polyhedron about Cu(2) whereas the other is appreciably longer. The orientation of the pyridine rings with respect to the equatorial plane is also different in the symmetrically independent polyhedra. The angles formed by the pyridine rings with the equatorial plane are 56° and 48° in the coordination polyhedron about Cu(2) and 127° and 154° in that about Cu(1). In the coordination polyhedron about Cu(3), both orientations of the pyridine rings occur, the angles are 49° and 134° .

The crystal structures of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ and $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ involve thiocyanatocopper(II) chains with different steric orientation. Whereas in the pyridine complex the chains are linear and mutually parallel⁸ (Fig. 2), only linear fragments (composed of three coordination polyhedra) with a zigzag arrangement occur in the

4-methylpyridine complex (Fig. 3). Only in the coordination polyhedron about Cu(2), lying in the centre of the linear fragment, the bonds are comparable to the coordination bonds in $[\text{Cu}(\text{py})_2(\text{NCS})_2]$, whereas in the coordination polyhedra about Cu(1) and Cu(3) the longer Cu—S bonds occur in sites where the orientation of the thiocyanatocopper(II) chain changes; these Cu—S bonds also exhibit significant differences in their length at 180 and 293 K (Table III). The differences in the orientation of the pyridine rings in the various coordination polyhedra are probably due to the steric effects of the nonlinear thiocyanatocopper(II) chains.

The results demonstrate that, as expected, the different electronic properties of 4-methylpyridine as compared to pyridine affect, via the central Cu(II) atom, the

FIG. 2
Orthogonal projection of the orientation of the thiocyanatocopper(II) chains in the crystal structure of $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ into the xz plane

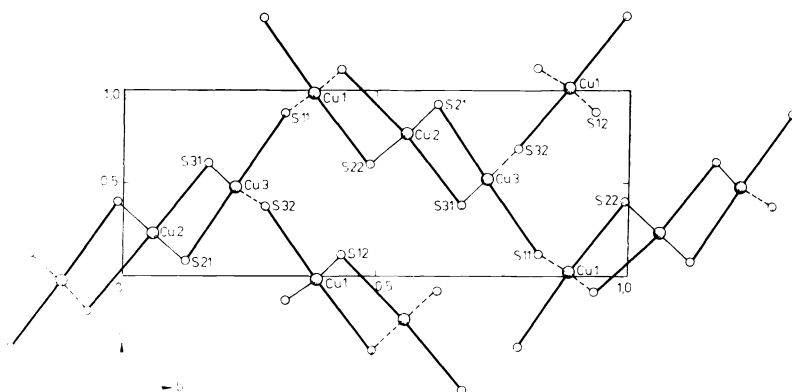
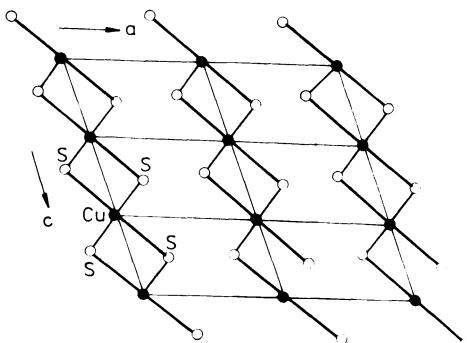


FIG. 3
Orthogonal projection of the orientation of the thiocyanatocopper(II) chains in the crystal structure of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ into the yz plane (elongated Cu—S bonds are shown by broken lines)

strength of the axial Cu—S bonds. Due to the elongation of the Cu—S bonds, the thiocyanatocopper(II) chains in the crystal structure of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ are no longer linear. Such changes in the crystal structure may stimulate a decrease in the redox stability of the thiocyanatocopper(II) chains during the thermal decomposition.

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