

THE CRYSTAL AND MOLECULAR STRUCTURE OF THIOCYANATO-COPPER(II) COMPLEXES WITH 3-METHYLPYRIDINE AND 3,4-DIMETHYLPYRIDINE

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Crystals of the complexes $[\text{Cu}(3,4\text{-diMepy})_3(\text{NCS})_2]$ (I) and $[\text{Cu}(3\text{-Mepy})_3(\text{NCS})_2]$ (II) (Me = methyl, py = pyridine) possess the monoclinic symmetry, Pc , with the unit cell parameters of I and II: $a = 0.9825(7)$ and $0.9027(7)$ nm, $b = 0.9740(7)$ and $0.9021(7)$ nm, $c = 1.4130(60)$ and $1.4958(50)$ nm, $\beta = 108.8(4)^\circ$ and $114.08(4)^\circ$, $Z = 2$ in both cases, $d_0 = 1.32 \cdot 10^3$ and $1.37 \cdot 10^3 \text{ kg m}^{-3}$, and $d_c = 1.30 \cdot 10^3$ and $1.37 \cdot 10^3 \text{ kg m}^{-3}$, respectively. The central atom in the complexes exhibits tetragonal pyramidal coordination. The thiocyanate ligands are coordinated by the nitrogen atoms in the equatorial as well as axial positions of the coordination polyhedron. The three heterocyclic ligands are bonded in the equatorial plane. The arrangement of the ligands and the interatomic distances are the same in the two complexes. The crystals were prepared by reacting an ammoniacal solution of CuSO_4 with an ethanolic solution of the heterocyclic ligand L and an aqueous solution of NH_4NCS so that the $c(\text{Cu}) : c(\text{NH}_3) : c(\text{L}) : c(\text{NCS})$ ratio was 2 : 8 : 5 : 4.

The bonding of the thiocyanate ligands in heterocyclic thiocyanatocopper(II) complexes depends on the bonding properties of the neutral ligands present in the coordination sphere of the copper¹. The neutral ligands affect the redox stability of the central atom²; in the case of thiocyanate ligands, a considerable stability lowering can emerge³. Our previous work gave evidence that in heterogeneous thiocyanatocopper(II) complexes, correlation can be obtained with the Cu—S interatomic distances in the axial direction of the coordination polyhedron. In the $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ complex (py = pyridine), the interatomic distance is 0.304 nm for all Cu—S bonds⁴; in the 4-methylpyridine complex, $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$, the Cu—S interatomic distances are 0.326 nm for one-sixth of the bonds, 0.311 nm for one-third of the bonds and 0.298 nm for one-half of the bonds⁵; in the 4-bromopyridine complex, $[\text{Cu}(4\text{-Brpy})_2(\text{NCS})_2]$, this interatomic distance is 0.308 nm for three-quarters of the bonds and 0.291 nm for one-quarter of the bonds⁶.

In the present work, the crystal structure is studied for the complexes with 3-methylpyridine and 3,4-dimethylpyridine, which should provide additional data for the dependence discussed, viz. for the case where three heterocyclic ligands occur in the coordination sphere.

EXPERIMENTAL

Green needle-shaped crystals of $[\text{CuL}_3(\text{NCS})_2]$ where $L = 3,4\text{-dimethylpyridine}$ or 3-methylpyridine (complexes *I* and *II*, respectively) were prepared by reacting an ammoniacal aqueous solution of CuSO_4 with an ethanolic solution of the ligand L and an aqueous solution of NH_4NCS so that the $c(\text{Cu}) : c(\text{NH}_3) : c(L) : c(\text{NCS})$ ratio was $2 : 8 : 5 : 4$. For $\text{Cu}(\text{C}_7\text{H}_9\text{N})_3(\text{NCS})_2$ (*I*) calculated: 55.11% C, 5.35% H, 12.68% Cu, 13.81% N; found: 55.00% C, 5.40% H, 12.65% Cu, 13.74% N. For $\text{Cu}(\text{C}_6\text{H}_7\text{N})_3(\text{NCS})_2$ (*II*) calculated: 52.32% C, 4.67% H, 13.79% Cu, 15.24% N; found: 52.39% C, 4.67% H, 13.81% Cu, 15.22% N.

Crude crystallographic data were obtained by the photographic Weissenberg oscillation method. Density of the crystals was measured by the floating method in a bromoform-ethanol mixture. Because of their low stability, crystals of the complexes were photographed in sealed-up Lindeman glass tubes containing vapours of the respective pyridine ligands. Lattice parameters were obtained by refining the positional angles for ten selected diffractions in a rotational Polaroid photograph obtained from a Syntex P2_1 diffractometer. The conditions were as follows. MoK_α radiation (0.071069), graphite monochromator, $\theta - 2\theta$ scanning technique, scan rate 4.89 to $29.3^\circ \text{ min}^{-1}$, crystal dimensions $0.2 \times 0.1 \times 0.5 \text{ mm}$ for *I* and $0.1 \times 0.6 \times 0.4 \text{ mm}$ for *II*, temperature 20°C , intensity checking by measuring intensities of two diffractions after each 98 diffractions, conditions for diffractions treated: $I \geq 2\sigma(I)$, number of diffractions observed: 1 580 for *I*, 1 390 for *II*. Standard diffraction intensity variations did not exceed 2%. The diffraction intensities were corrected for the Lorentz polarization factor and absorption, viz. by scanning for selected diffractions.

The crystal structure was elucidated by the heavy atom method. The position of the Cu atom was determined by Patterson synthesis, the positions of the remaining non-hydrogen atoms. by Fourier synthesis. The positions of the methyl group hydrogen atoms were calculated from differential Fourier syntheses, the remaining positions were added based on the sp^2 and sp^3 hybridization concept. The crystal structures were refined in both the isotropic and anisotropic approximations by the least squares method with the complete matrix. The ultimate values of $R = 0.065$

TABLE I

Crystallographic data of complexes *I* and *II*. Both crystallize in the monoclinic system, space group Pc , $Z = 2$. Data in parentheses are standard deviations

Parameter	<i>I</i>	<i>II</i>
a , nm	0.9825(7)	0.9027(7)
b , nm	0.9740(7)	0.9021(7)
c , nm	1.4130(60)	1.4958(50)
β , deg	108.80(0.4)	114.08(0.4)
V , nm ³	1.2800(64)	1.1121(52)
d_0 , 10^3 kg m^{-3}	1.32(1)	1.37(1)
d_c , 10^3 kg m^{-3}	1.30	1.37
$\mu(\text{MoK}_\alpha)$, mm^{-1}	10.6	12.2
$F(000)$	522	490

TABLE II

Fractional coordinates of non-hydrogen atoms in complexes *I* and *II* and their temperature factors $B_{eq} = 8/3\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$; standard deviations are given in parentheses

Atom	<i>I</i>				<i>II</i>			
	(<i>x/a</i>) · 10 ⁴	(<i>y/b</i>) · 10 ⁴	(<i>z/c</i>) · 10 ⁴	<i>B</i> _{eq} · 10 ⁻⁴ nm ²	(<i>x/a</i>) · 10 ⁴	(<i>y/b</i>) · 10 ⁴	(<i>z/c</i>) · 10 ⁴	<i>B</i> _{eq} · 10 ⁻⁴ nm ²
Cu1	1 220(0)	404(1)	5 158(0)	380(4)	1 220(0)	248(1)	5 158(0)	418(3)
S1	1 550(6)	-2 265(5)	2 267(4)	818(18)	1 846(4)	-2 200(4)	2 394(3)	897(15)
S2	5 859(6)	2 334(7)	5 910(7)	1 214(27)	6 257(4)	276(5)	6 419(3)	955(14)
N1	1 155(16)	-556(14)	3 723(10)	730(46)	1 154(12)	-632(11)	3 775(7)	795(40)
N2	3 122(13)	1 286(12)	5 415(9)	582(41)	3 363(11)	1 221(9)	5 641(6)	634(36)
N3	2 234(13)	-1 186(13)	6 054(11)	587(46)	2 265(9)	-1 600(10)	5 965(7)	529(32)
N4	-708(12)	-318(12)	5 068(9)	567(38)	-964(9)	-479(9)	4 995(6)	555(30)
N5	294(13)	2 155(12)	4 484(9)	543(39)	205(12)	2 228(11)	4 559(8)	655(39)
C1	1 317(14)	-1 298(14)	3 121(10)	500(45)	1 458(12)	-1 285(12)	3 205(8)	574(43)
C2	4 246(16)	1 714(14)	5 621(10)	532(49)	4 585(14)	1 878(13)	5 962(7)	582(44)
C31	2 062(16)	-2 440(19)	5 685(13)	701(57)	3 028(13)	-1 508(12)	6 934(10)	653(44)
C32	2 822(22)	-3 596(16)	6 257(19)	797(79)	3 739(14)	-2 735(17)	7 543(9)	675(50)
C33	3 634(22)	-3 324(27)	7 236(19)	891(82)	3 652(16)	-4 049(19)	7 084(13)	926(66)

C34	3 755(18)	- 2 034(24)	7 565(14)	776(63)	2 876(17)	- 4 178(15)	6 077(12)	908(64)
C35	3 115(16)	- 991(18)	6 992(11)	664(52)	2 205(14)	- 2 905(15)	5 546(9)	733(46)
C36	4 347(29)	- 4 543(26)	7 969(24)	1 435(24)	4 569(18)	- 2 616(18)	8 609(10)	1 104(72)
C37	2 753(29)	- 4 943(21)	5 805(17)	1 058(97)	-	-	-	-
C41	- 1 080(17)	- 665(16)	5 894(12)	672(55)	- 1 369(11)	- 739(10)	5 741(7)	540(36)
C42	- 2 500(21)	- 1 193(16)	5 780(16)	712(65)	- 2 854(11)	- 1 247(13)	5 653(8)	560(39)
C43	- 3 429(17)	- 1 341(18)	4 864(14)	701(59)	- 3 987(13)	- 1 468(17)	4 713(11)	809(52)
C44	- 3 067(18)	- 1 043(21)	4 076(16)	817(59)	- 3 622(16)	- 1 272(16)	3 941(9)	776(54)
C45	- 1 711(17)	- 542(16)	4 194(13)	664(60)	- 2 090(13)	- 789(12)	4 102(8)	642(38)
C46	- 4 923(23)	- 1 931(26)	4 759(22)	1 160(105)	- 3 142(15)	- 1 524(20)	5 671(10)	950(75)
C47	- 2 826(21)	- 1 461(25)	6 713(14)	953(81)	-	-	-	-
C51	- 606(14)	2 911(13)	4 819(10)	541(41)	- 689(16)	3 042(14)	4 904(9)	750(48)
C52	- 1 177(16)	4 141(18)	4 415(12)	665(54)	1 330(18)	4 386(14)	4 512(13)	969(63)
C53	- 802(18)	4 691(16)	3 594(12)	664(55)	- 1 052(26)	4 900(15)	3 704(16)	1 240(90)
C54	105(20)	3 870(16)	3 248(12)	726(58)	- 208(22)	4 091(16)	3 335(11)	1 022(74)
C55	646(18)	2 687(18)	3 708(13)	695(53)	404(14)	2 785(15)	3 780(10)	777(55)
C56	- 1 404(23)	5 974(22)	3 070(17)	952(77)	- 2 138(39)	5 289(30)	4 902(28)	1 311(168)
C57	- 1 971(25)	5 011(20)	4 911(19)	430(29)	- 321(29)	4 550(27)	2 444(19)	891(106)

TABLE III
Interatomic distances and angles in crystals of complexes *I* and *II*

Atoms	Interatomic distance, nm		Atoms	Angle, °	
	<i>I</i>	<i>II</i>		<i>I</i>	<i>II</i>
Cu1-N1	0.222(2)	0.219(1)	N4-Cu1-N5	89.6(0.5)	89.4(0.4)
Cu1-N2	0.198(1)	0.197(1)	N2-Cu1-N5	170.5(0.5)	170.9(0.4)
Cu1-N3	0.205(1)	0.205(1)	N3-Cu1-N4	92.1(0.5)	89.9(0.3)
Cu1-N4	0.198(1)	0.200(1)	N2-Cu1-N5	88.6(0.5)	88.2(0.4)
Cu1-N5	0.202(1)	0.204(1)	N2-Cu1-N4	171.6(0.6)	164.3(0.4)
S1-C1	0.160(2)	0.162(1)	N2-Cu1-N3	88.4(0.5)	89.9(0.3)
S2-C2	0.162(2)	0.160(1)	N1-Cu1-N5	92.8(0.5)	93.9(0.4)
N1-C1	0.117(2)	0.116(2)	N1-Cu1-N4	92.6(0.5)	96.9(0.4)
N2-C2	0.113(2)	0.117(2)	N1-Cu1-N3	96.4(0.5)	95.2(0.4)
N3-C31	0.131(2)	0.133(2)	N1-Cu1-N2	95.6(0.6)	98.7(0.4)
N3-C35	0.134(2)	0.132(2)	S1-C1-N1	177.6(1.4)	178.9(1.0)
N4-C41	0.137(2)	0.133(2)	S2-C2-N2	179.6(1.0)	179.0(1.0)
N4-C45	0.133(2)	0.134(1)	N3-C31-C32	121.6(1.5)	123.5(1.1)
N5-C51	0.135(2)	0.134(1)	C31-C32-C33	116.0(1.8)	116.2(1.2)
N5-C55	0.136(3)	0.135(2)	C32-C33-C34	119.2(2.0)	121.6(1.4)
C31-C32	0.145(3)	0.141(2)	C33-C34-C35	122.7(1.7)	117.6(1.4)
C32-C33	0.138(3)	0.136(2)	C34-C35-N3	121.5(1.6)	122.7(1.2)
C32-C37	0.145(3)	—	N4-C41-C42	120.3(1.4)	124.8(0.8)
C33-C34	0.133(4)	0.138(2)	C41-C42-C43	118.8(2.0)	115.9(1.2)
C33-C36	0.158(4)	—	C42-C43-C44	121.1(1.8)	121.5(1.2)
C34-C35	0.133(3)	0.139(2)	C43-C44-C45	119.6(1.6)	118.5(1.1)
C32-C36	—	0.146(2)	C44-C45-N4	124.8(1.8)	122.8(1.2)
C41-C42	0.146(3)	0.137(2)	N5-C51-C52	124.1(1.5)	122.5(1.5)
C42-C43	0.133(3)	0.138(2)	C51-C52-C53	119.2(1.6)	117.8(1.7)
C42-C47	0.148(3)	—	C52-C53-C54	115.4(1.4)	120.6(1.4)
C42-C46	—	0.152(2)	C53-C54-C55	121.2(1.8)	117.5(1.8)
C43-C44	0.131(3)	0.134(2)	C54-C55-N5	123.7(1.8)	125.3(1.5)
C43-C46	0.154(3)	—			
C44-C45	0.138(3)	0.137(2)			
C51-C52	0.137(2)	—			
C52-C56	—	0.137(4)			
C52-C43	0.143(3)	0.141(3)			
C52-C57	0.147(3)	—			
C53-C54	0.140(3)	0.133(3)			
C53-C56	0.148(3)	—			
C54-C55	0.135(2)	0.136(2)			
Cu1-S1	0.341(1)	0.362(1)			

and $R = 0.054$ were obtained for *I* and *II*, respectively, the weighted values R_w for $w = 1/\sigma^2(F)$ were 0.068 and 0.054, respectively. The dispersion curves of the neutral atoms were taken from the International Tables; correction for anomalous dispersion⁷ was made for the Cu atom. Calculations were performed on a NOVA 1 200 computer using the XTL program⁸ and on a MINSK-M-4030-1 computer using the SHELX 76 and PARST programs^{9,10}.

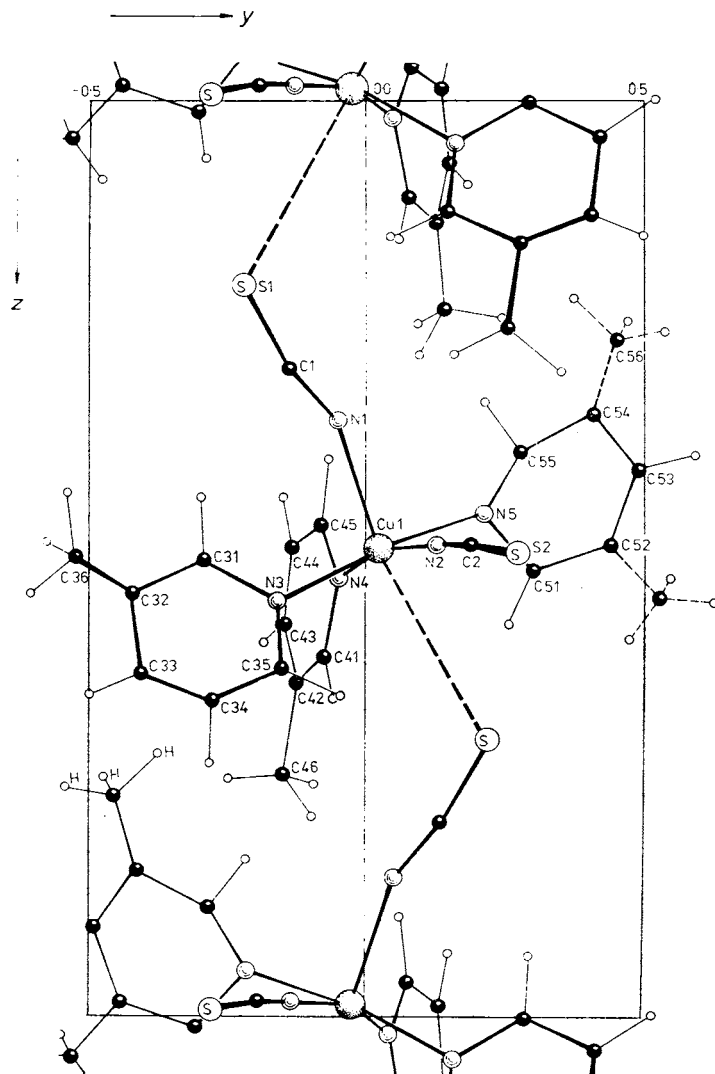


FIG. 1

Orthogonal projection of the crystal structure of $[\text{Cu}(3\text{-Mepy})_3(\text{NCS})_2]$ in the yz plane. The methyl substituent at the heterocyclic ring with N5 has the statistical orientation $g_1 = 0.56$ and $g_2 = 0.44$

RESULTS AND DISCUSSION

The two complexes *I* and *II* crystallize in the monoclinic system, *Pc*, $Z = 2$. Their crystallographic data are given in Table I. The fractional coordinates of the non-hydrogen atoms in *I* and *II* are given in Table II, the interatomic distances and angles, in Table III. The observed and calculated structure factors, anisotropic

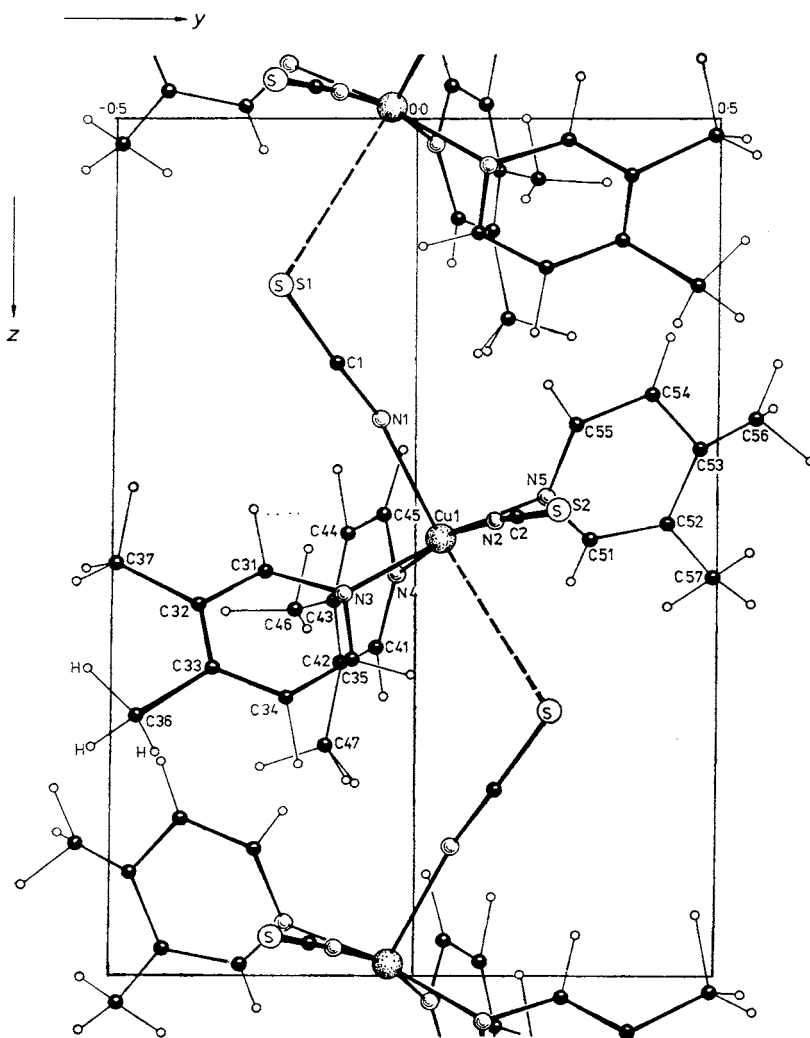


FIG. 2

Orthogonal projection of the crystal structure of $[\text{Cu}(3,4\text{-diMepy})_3(\text{NCS})_2]$ in the yz plane

temperature factors, fractional coordinates of hydrogen atoms and their interatomic distances can be obtained from the authors on request.

In the crystal structures elucidated (Figs 1 and 2), the central atom has a tetragonal pyramidal coordination and the chromophore is CuN_5 . Three heterocyclic ligands and one thiocyanate ligand are coordinated by four nitrogen atoms in the equatorial plane. The other thiocyanate ligand is coordinated in the axial position also by the nitrogen atom. The angles between the planes formed by the aromatic rings and the plane formed by the nitrogen atoms in the equatorial plane are $55.6(0.4)^\circ$, $57.5(0.5)^\circ$ and $60.4(0.5)^\circ$ in *I* and $69.1(0.5)^\circ$, $114.2(0.4)^\circ$ and $69.2(0.5)^\circ$ in *II*. The thiocyanate ligands are all virtually linear in the two complexes.

The results indicate that the oxidation state of copper is stabilized by the presence of the three heterocyclic ligands in its coordination sphere to such an extent that coordination of sulfur atoms is excluded from the primary coordination sphere. At the fifth coordination site, a thiocyanate ligand is coordinated by its nitrogen atom, and at the sixth coordination site the distance of the sulfur atoms from copper is so long that they are subject to intermolecular interactions. It is noteworthy that even so far away from the copper atom, the Cu—S interatomic distance is affected by the differences in the bonding properties of 3-methylpyridine and 3,4-dimethylpyridine, this distance being 0.02 nm longer in *II* than in *I*. This effect is also apparent in their infrared spectra, on the $\nu(\text{CN})$ stretching vibrations in particular¹¹: their wavenumbers are 2 084 and 2 143 cm^{-1} for *I* and 2 062 and 2 088 cm^{-1} for *II*.

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