Structural Research on Mixed Thiocyanate Copper(II) Complexes with Multidentate Ligands containing Nitrogen as the Donor Atom. Crystal and Molecular Structures of Isothiocyanato[*NN*′-bis(2-pyridylmethylene)tetramethylenediamine]copper(II) Thiocyanate and of Bis(isothiocyanato)[2-(2-pyridyl)benzimidazole]copper(II)

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The structures of the title compounds have been determined from *X*-ray diffraction data by the heavy-atom method and refined by least squares. Crystal data: $[Cu(C_{16}H_{18}N_4)NCS]SCN$, (I), $a = 13.93(1)$, $b = 9.78(1)$, $c = 15.06(1)$ Å, $\beta = 96.8(1)°$, $Z = 4$, space group $P2_1/c$, final R 6.7%; $[Cu(C_{12}H_9N_3)(NCS)_2]$, (II), $a = 14.96(1)$, $b = 12.23(1)$, $c = 8.57(1)$ Å, $\beta = 106.8(1)°$, $Z = 4$, space group $P2_1/n$, final R 4.3%. In (I) the copper co-ordination is trigonal bipyramidal and involves five nitrogen atoms, one from a thiocyanate group (Cu–N 1.99 Å) and the four nitrogen atoms of the organic ligand (Cu–N 2.03, 1.99, 2.00, and 2.19 Å). One thiocyanate group is ionic and has no direct interaction with the metal. In (II) the co-ordination polyhedron is a nearly regular tetragonal pyramid formed by two nitrogen atoms from the organic ligand (Cu–N 2.05 and 1.97 Å) and two from two thiocyanate groups (Cu–N 1.95 and 1.94 Å) in the basal plane with a sulphur atom from one thiocyanate group (Cu–S 2.95 Å) at the apex.

THE crystal structure analyses of (I), [Cu(pmtmd)(NCS)](SCN), [pmtmd = *NN*′-bis(2-pyridylmethylene)tetramethylenediamine] and (II), $[Cu(pbi)(NCS)_2]$, [pbi = 2-(2-pyridyl)benzimidazole] are part of our research on copper(II) complexes with ligands containing α-di-imine groups.[1-3] We wished to investigate ligand behaviour and co-ordination geometry which could not be deduced with confidence from chemical and spectral data alone.

EXPERIMENTAL

Preparation of (I).—Copper chloride dihydrate (0.02 mol), 1,4-tetramethylenediamine (0.02 mol) and 2-picolinaldehyde (0.04 mol) were heated under reflux with stirring in ethanol solution for 4—5 h. Slow evaporation of the solvent gave a green microcrystalline product $[Cu(pmtmd)Cl_2]$. When this was treated with potassium thiocyanate (molar ratio 1 : 2) in ethanol [Cu(pmtmd)NCS]SCN was obtained, and crystallized from ethanol as green platelets (Found: C, 48.2; H, 4.25; Cu, 14.1; N, 19.3. Calc. for $C_{18}H_{18}CuN_6S_2$: C, 48.5; H, 4.1; Cu, 14.25; N, 18.85%).

Preparation of (II).—Copper acetate monohydrate (0.02 mol) was heated under reflux in ethanol solution with the product obtained by condensation of *o*-phenylenediamine (0.02 mol) with 2-picolinaldehyde (0.04 mol). After 2 h a grey-green product $[Cu(C_{18}H_{14}N_4)(MeCO_2)_2]$ was isolated from the warm solution. This was dissolved in acetone-water with some acetic acid, and heated under reflux with potassium thiocyanate (molar ratio 1 : 2), to yield, by slow evaporation of the solvent, deep-green prismatic crystals of $[Cu(pbi)(NCS)_2]$ (Found: C, 44.95; H, 2.4; Cu, 16.9; N, 18.5. Calc. for $C_{14}H_9CuN_5S_2$: C, 44.85; H, 2.4; Cu, 17.0; N, 18.7%).

During formation of the thiocyanate complex the organic molecule undergoes hydrolysis and oxidation to form the benzimidazole ligand. The mechanism is not clear, but it is probable that the hydrolysis process produces dihydrobenzimidazole, which is oxidized successively to benzimidazole. These processes are probably catalyzed by the copper ion.[4,5]

Physical Measurements.—I.r. spectra were measured on a Perkin-Elmer 457 spectrophotometer (KBr disc). *X*-Ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer by the ω—2θ scan technique.

Crystal Data.—(I). $C_{18}H_{18}CuN_6S_2$, $M = 446.05$, Monoclinic, $a = 13.93(1)$, $b = 9.78(1)$, $c = 15.06(1)$ Å, $\beta = 96.8(1)°$, $U = 2\,036$ Å^3, $D_m = 1.47$ g cm^{-3}, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 916$. Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 34.9$ cm^{-1}. Space group $P2_1/c$ (from systematic absences).

(II). $C_{14}H_9CuN_5S_2$, $M = 374.94$, Monoclinic, $a = 14.96(1)$, $b = 12.23(1)$, $c = 8.57(1)$ Å, $\beta = 106.8(1)°$, $U = 1\,501$ Å^3, $D_m = 1.702$ g cm^{-3}, $Z = 4$, $D_c = 1.673$ g cm^{-3}, $F(000) = 756$. Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 45.5$ cm^{-1}. Space group $P2_1/n$ (from systematic absences).

For both compounds, cell dimensions were determined from rotation and Weissenberg photographs and refined by least-squares fits to the $(\theta, \chi, \phi)_{hkl}$ values for 12 and 14 reflections respectively measured on the diffractometer.

Data Collection.—For both compounds all the reflections with $2\theta \leqslant 100°$ for (I) and $\leqslant 140°$ for (II) were collected; in this way 2 098 independent reflections were measured for (I) and 2 287 for (II), of which 1 506 and 1 820 respectively, having $I > 2\sigma(I)$, were considered observed and used in the subsequent analysis. After the usual data reduction, the intensities were put on an absolute scale, first by Wilson's method,[6] then by comparison between observed and calculated values. No correction for absorption was made as the samples were sufficiently small [crystal sizes: (I) 0.048 × 0.119 × 0.333 mm, and (II) 0.024 × 0.090 × 0.119 mm].

Structure Analyses.—Both structures were solved by the heavy-atom technique starting from the three-dimensional Patterson distributions. Successive Fourier syntheses

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[1] M. Belicchi Ferrari, A. Bonamartini Corradi, G. Gasparri Fava, C. Grasselli Palmieri, M. Nardelli, and C. Pelizzi, *Acta Cryst.*, 1973, **B29**, 1808.

[2] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *Acta Cryst.*, 1974, **B30**, 17.

[3] A. Mangia, C. Pelizzi, and G. Pelizzi, *Acta Cryst.*, 1974, **B30**, 2146.

[4] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *J.C.S. Dalton*, 1972, 2483.

[5] A. C. Braithwaite, C. E. F. Rickard, and T. N. Waters, *J.C.S. Dalton*, 1975, 2149.

[6] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

gave the co-ordinates of all non-hydrogen atoms which were refined by means of isotropic and anisotropic least-squares calculations, the function minimized being $\Sigma w|\Delta F|^2$. For (II) weights were derived from the $|\Delta F|$ *vs.* $|F_o|$ distribution and the final value of R was 5.6%. For (I) unit weights were used and the final value of R was 7.0%. At this point a difference-Fourier map of (I) revealed two distinct peaks for C(9) indicating a disordered distribution of this atom between two positions. The populations of these positions, as estimated from the difference synthesis, were introduced in further isotropic least-squares calculations which led to R 6.7% (including the hydrogen atoms in calculated positions, except those of the C(9) atom which were not considered). For (II) hydrogen atoms were directly located from a ΔF synthesis and the isotropic refinement led to R 4.3%.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms, with estimated standard deviations in parentheses, for (I)

	x/*a*	*y*/*b*	*z*/*c*
Cu	2 745(1)	1 890(1)	64(1)
S(1)	4 794(2)	4 609(4)	1 980(2)
S(2)	2 144(3)	6 880(4)	1 715(3)
N(1)	3 411(5)	71(8)	103(5)
N(2)	1 395(5)	1 374(8)	592(4)
N(3)	2 045(5)	3 661(8)	−89(5)
N(4)	2 614(5)	1 483(8)	−1 266(5)
N(5)	3 624(6)	2 659(9)	1 076(5)
N(6)	209(7)	6 359(12)	1 371(6)
C(1)	3 818(7)	−598(11)	832(7)
C(2)	4 262(7)	−1 881(11)	764(7)
C(3)	4 291(7)	−2 460(11)	−81(8)
C(4)	3 870(7)	−1 745(11)	−827(7)
C(5)	3 437(6)	−490(10)	−721(6)
C(6)	2 979(7)	351(10)	−1 458(7)
C(7)	2 129(8)	2 387(11)	−1 976(6)
C(8)	2 683(8)	3 731(12)	−2 026(7)
C(10)	2 464(9)	4 896(11)	−496(7)
C(11)	1 250(7)	3 763(11)	238(6)
C(12)	870(7)	2 512(11)	630(6)
C(13)	−8(8)	2 573(13)	1 021(7)
C(14)	−317(8)	1 352(14)	1 354(7)
C(15)	208(8)	163(12)	1 314(7)
C(16)	1 092(7)	185(11)	918(6)
C(17)	4 101(7)	3 497(11)	1 455(6)
C(18)	1 007(8)	6 585(12)	1 526(7)
C(9A) *	2 249(15)	4 956(23)	−1 437(14)
C(9B) †	3 010(36)	4 507(55)	−1 285(33)

* Occupancy 0.75. † Occupancy 0.25.

TABLE 2

Calculated fractional co-ordinates ($\times 10^3$) and calculated thermal parameters ($\times 10$ Å^2) for hydrogen atoms of (I)

	x/*a*	*y*/*b*	*z*/*c*	*B*
H(1)	381	−17	144	49
H(2)	455	−238	131	55
H(3)	461	−337	−15	54
H(4)	388	−214	−144	50
H(6)	296	4	−209	43
H(7)	210	191	−257	50
H(7′)	146	259	−184	50
H(8)	338	357	−179	53
H(8′)	264	402	−267	53
H(10)	317	493	−30	54
H(10′)	215	573	−28	54
H(11)	90	465	23	47
H(13)	−38	344	106	54
H(14)	−93	133	163	58
H(15)	−3	−71	156	53
H(16)	148	−67	88	46

Hydrogen atoms are numbered according to the carbon atoms to which they are attached.

Positional parameters with their estimated standard deviations are given in Tables 1—4 for the two structures.

TABLE 3

Final atomic fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms, with estimated standard deviations in parentheses, for (II)

	x/*a*	*y*/*b*	*z*/*c*
Cu	96(1)	2 192(0)	250(1)
S(1)	−1 726(1)	−965(1)	84(1)
S(2)	−1 657(1)	1 448(1)	−4 979(2)
N(1)	707(3)	2 231(3)	2 720(4)
N(2)	764(2)	3 595(2)	416(3)
N(3)	1 641(3)	4 862(2)	2 019(4)
N(4)	−690(3)	962(3)	444(5)
N(5)	−500(3)	2 268(3)	−2 080(5)
C(1)	621(4)	1 489(3)	3 803(5)
C(2)	1 022(4)	1 635(4)	5 459(5)
C(3)	1 501(3)	2 577(4)	6 014(5)
C(4)	1 610(3)	3 348(4)	4 905(5)
C(5)	1 201(3)	3 140(3)	3 255(4)
C(6)	1 222(3)	3 872(3)	1 929(4)
C(7)	1 437(3)	5 249(3)	434(4)
C(8)	888(3)	4 455(3)	−568(4)
C(9)	566(3)	4 602(3)	−2 250(4)
C(10)	821(3)	5 571(4)	−2 847(5)
C(11)	1 358(4)	6 365(4)	−1 837(6)
C(12)	1 681(3)	6 226(3)	−169(5)
C(13)	−1 120(3)	162(3)	280(4)
C(14)	−982(3)	1 928(3)	−3 280(5)

TABLE 4

Final fractional co-ordinates ($\times 10^3$) and thermal parameters ($\times 10$ Å^2) for hydrogen atoms, with estimated standard deviations in parentheses for (II)

	x/*a*	*y*/*b*	*z*/*c*	*B*
H(1)	32(3)	90(3)	336(5)	36(9)
H(2)	89(3)	120(4)	612(5)	49(11)
H(3)	169(3)	267(3)	705(5)	44(10)
H(4)	196(3)	406(3)	525(5)	39(9)
H(9)	10(3)	408(3)	−291(4)	30(8)
H(10)	59(3)	572(4)	−391(6)	56(11)
H(11)	146(4)	703(4)	−237(6)	54(12)
H(12)	207(3)	678(3)	55(5)	33(9)
H(13)	208(3)	503(3)	277(5)	28(9)

Hydrogen atoms are numbered according to the carbon atom to which they are attached, except H(13) which is attached to N(3).

Observed and calculated structure factors and anisotropic thermal parameters are given in Supplementary Publication No. SUP 21761 (22 pp., 1 microfiche).* Atomic scattering factors used throughout the calculations were taken from ref. 7 for non-hydrogen atoms and from ref. 8 for hydrogen atoms.

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale with programs of Immirzi.[9]

RESULTS AND DISCUSSION

As shown by the clinographic projection of (I) (Figure 1), the co-ordination around copper is trigonal bipyrami-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index ssue.

[7] D. T. Cromer and G. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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dal and involves five nitrogen atoms, four from the organic ligand and one from the thiocyanate group. The copper atom shows only a small displacement (0.03 Å) from the equatorial plane of the bipyramid. This type of co-ordination is characterized by a small but significant shortening of the distances involving the apical nitrogen atoms, with respect to the corresponding ones in the equatorial plane (Figure 2). This flattening of the bipyramid, which can be justified on the basis of the electron-pair repulsion model of Gillespie,[10] has been already observed for other similar copper complexes with quadridentate [1,11,12] and bidentate ligands [13-15] with nitrogen as donor atoms. No abnormal lengthening is observed for the distance involving the thiocyanate nitrogen.

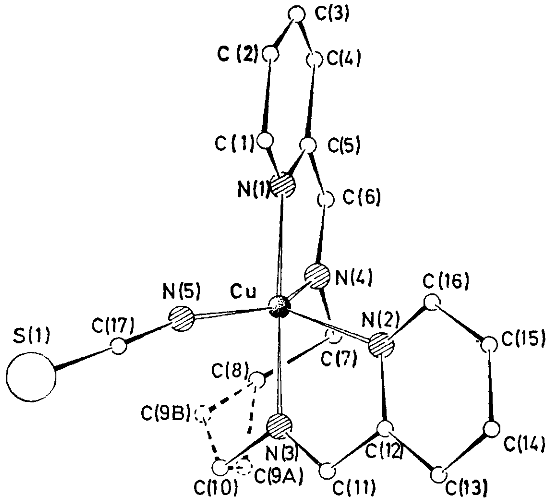

FIGURE 1 Clinographic projection of [Cu(pmtmd)(NCS)]$^+$

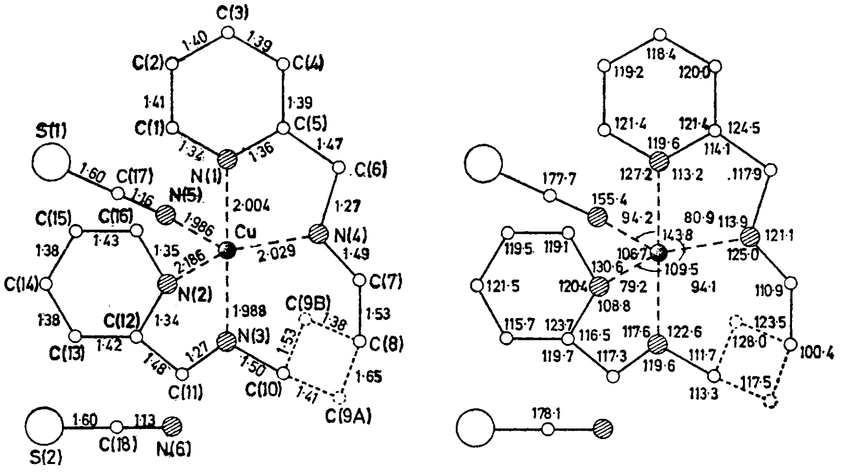

FIGURE 2 Bond distances (Å) and angles (°) for (I). Mean σ for distances: Cu–N 0.008, C–S, C–N 0.01, C–C 0.02 [0.04 Å for those involving C(9A) and C(9B)]. Mean σ for angles: N–Cu–N 0.3, Cu–N–C 0.7; angles involving C(9A) and C(9B) 2.2, all other angles 0.90

The quadridentate ligand makes three chelation rings: one seven-membered: [Cu,N(4),C(7)—(10), N(3)], and two five-membered: [Cu,N(1),C(5),C(6),N(4)] and [Cu,-N(2), C(11), C(12), N(3)]. The C(9) atom is statistically distributed between two positions (Figure 1) corresponding to two different conformations (chair and boat) assumed by the seven-membered ring. The two five-membered rings are not strictly planar, the copper atom being 0.007 and 0.195 Å out of the planes of the other four atoms (Table 5) respectively.

TABLE 5

Equations of some least-squares best planes (in orthogonal Å co-ordinates) and deviations (Å) of relevant atoms from them in square brackets

Complex (I)

Plane (1): N(1), C(5), C(6), N(4)

$$0.8885X + 0.4536Y - 0.0699Z = -4.2259$$

[Cu 0.007]

Plane (2): N(2), C(11), C(12), N(3)

$$-0.3980X - 0.2237Y - 0.8897Z = 1.8208$$

[Cu 0.195]

Complex (II)

Plane (3): N(2), N(3), C(6)—(8)

$$0.8919X - 0.4407Y - 0.1011Z = -1.0441$$

[N(2) −0.0007(35), N(3) −0.0008(38), C(6) 0.0011(44), C(7) 0.0002(44), C(8) 0.0002(43)]

Plane (4): N(2), N(3), C(6)—(12)

$$0.8952X - 0.4344Y - 0.0996Z = -1.0021$$

The N(3) and N(4) atoms are trigonal, as the bonds N(3)–C(11) and N(4)–C(6) (1.27 Å) are mainly double in

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[10] R. J. Gillespie, *J. Chem. Soc.*, 1963, 4679.

[11] A. Corradi, P. Domiano, G. Fava, C. Guastini, and M. Nardelli, *Coll. Abs.* 2nd European Crystallographic Meeting, Keszthely, Hungary, 1974, 855.

[12] P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 6131.

[13] M. Cannas, G. Carta, and G. Marongiu, *J.C.S. Dalton*, 1974, 550.

[14] M. Belicchi Ferrari, G. Gasparri Fava, and A. Montenero, *Cryst. Struct. Comm.*, 1975, **4**, 577.

[15] J. E. Johnson and R. A. Jacobson, *J.C.S. Dalton*, 1973, 580.

character [calc.[16] for C(sp^2)=N(sp^2) 1.265 Å]. The two pyridine rings are planar and their bond distances and angles are as expected (Figure 2).

The thiocyanate ions are differently situated: N(5),-C(17),S(1) co-ordinates to copper through nitrogen, while N(6),C(18),S(2) is not co-ordinated (Figure 3) and this is probably a consequence of the quadridentate character of the bulky organic ligand which leaves only one position for further co-ordination.

Packing is determined by van der Waals contacts; the shortest contact involves the unco-ordinated thiocyanate nitrogen.

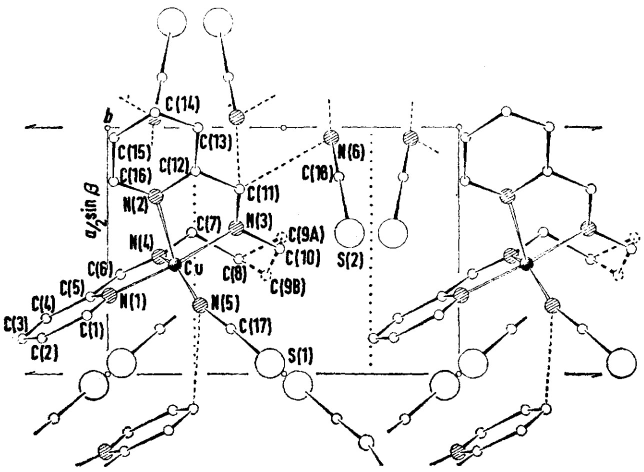

FIGURE 3 Projection of (I) on the (001) plane

In (II) the copper co-ordination is square planar with slight tetrahedral distortions, and involves two nitrogen atoms of the organic ligand and the nitrogen atoms of the two thiocyanate groups (Figure 4). The co-ordination polyhedron is completed, to a nearly regular tetragonal pyramid, by the sulphur of one thiocyanate group from an adjacent complex molecule. As is usually observed with this type of co-ordination, the copper is out of the co-ordination plane (0.12 Å) in the direction of the apical sulphur atom. A sixth co-ordination position involves a long interaction (3.23 Å) between copper and the C(11)-C(12) bond of an adjacent benzene ring. Co-ordination on the whole can therefore be considered as tetragonally distorted octahedral. The Cu-N(NCS) distances, which are not significantly different, are sensibly shorter than the Cu-N(pyridine) distance, which is itself significantly longer than the Cu-N(imidazole) distance (Figure 5). These differences can be related to the greater π-acceptor character of the imidazole nitrogen with respect to the pyridine nitrogen and to the different hybridization of the thiocyanate nitrogen.[17,18] The Cu-S distance is of the same order of magnitude as in complexes where sulphur is not strongly co-ordinated.[19]

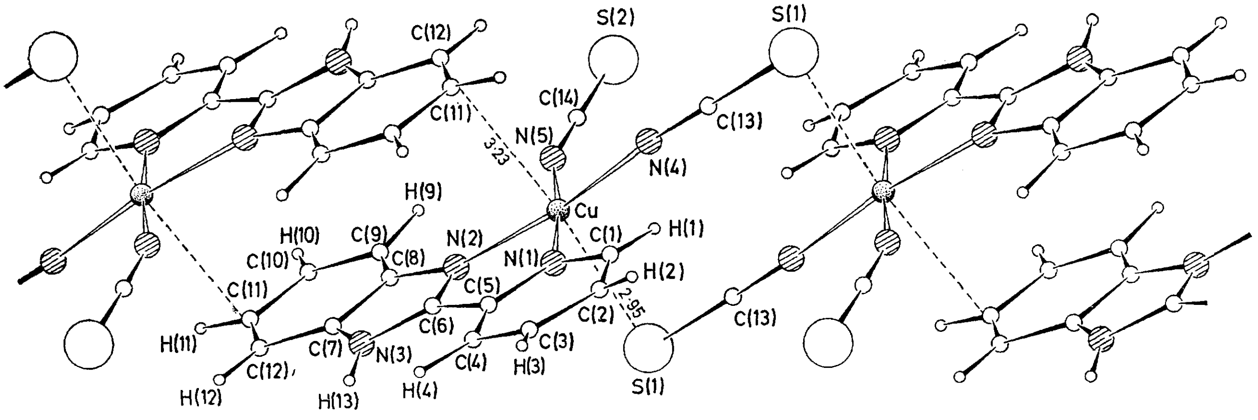

FIGURE 4 Projection of (II) on the (001) plane

The imidazole moiety is perfectly planar [plane (3), Table 5], and the benzene and imidazole rings are coplanar.

The whole organic ligand is nearly planar: the distortion from planarity involves the pyridine moiety which is slightly 'boat', distorted as shown by the following torsion angles (°):

C(5)-N(1)-C(1)-C(2)	0.39	C(2)-C(3)-C(4)-C(5)	1.67
N(1)-C(1)-C(2)-C(3)	1.72	C(3)-C(4)-C(5)-N(1)	0.45
C(1)-C(2)-C(3)-C(4)	2.72	C(4)-C(5)-N(1)-C(1)	1.48

and the benzimidazole plane which forms a dihedral angle of 179.1° with the pyridine plane. Bond distances and angles in the pyridine and in the benzene rings agree well with literature values. Bond distances and angles in the imidazole moiety are in agreement with the resonance structures (A) and (B) suggested by Harkins *et al.*[20] and by Chiswell *et al.*[21] from spectroscopic evidence for metal chelates of imidazole derivatives.

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[16] J. Donohue, L. R. Lavine, and J. S. Rollett, *Acta Cryst.*, 1956, **3**, 655.

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[18] U. A. Gregory, J. A. J. Jarris, B. T. Killbourn, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 2770.

[19] M. Belicchi Ferrari, L. Calzolari Capacchi, G. Gasparri Fava, A. Montenero, and M. Nardelli, *Kristallografiya*, 1972, **17**, 22.

[20] R. T. Harkins, J. H. Walter, O. T. Harris, and H. Freiser, *J. Amer. Chem. Soc.*, 1956, **78**, 260.

[21] B. Chiswell, F. Lions, and B. S. Morris, *Inorg. Chem.*, 1964, **3**, 110.

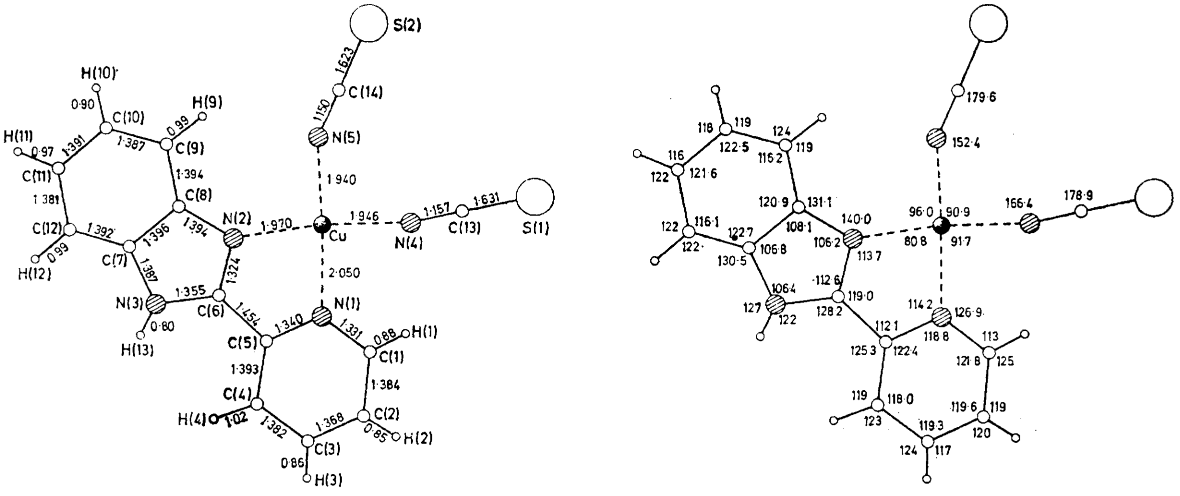
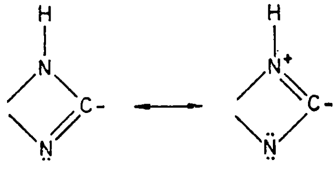


FIGURE 5 Bond distances (Å) and angles (°) for (II). Mean σ for distances: Cu–N, N–C, C–S 0.005, C–C 0.006, those involving H atoms 0.04 Å. Mean σ for angles: N–Cu–N 0.2, Cu–N–C, N–C–C, N–C–N, C–C–C 0.3, angles involving H atoms 3°

Both thiocyanate groups are co-ordinated to the metal through nitrogen, but one of them [N(4),C(13),S(1)] forms an additional long contact through its sulphur atom to the metal atom of an adjacent molecule giving a very asymmetric bridge. The preferred co-ordination through nitrogen, as observed also for (I), is indicative of the 'hard' character of copper in agreement with its oxidation state and with the π-acceptor character of the organic ligand. Table 6 gives a comparison of bond distances and angles involving copper(II) thiocyanate complexes, and shows: (i) the distances C–S and C–N are not significantly influenced by co-ordination, (ii) the angle S–C–N always deviates slightly from linearity, (iii) the angles Cu–N–C in both (I) and (II) are at the lower limit of the range of those reported in the literature, and (iv) for the bridging SCN the Cu–S–C angle is in the range found for compounds where thiocyanate is *S*-co-ordinated to the metal.



(A) (B)

TABLE 6

Comparison of bond distances (Å) and angles (°) in copper(II) thiocyanate complexes

C–S	C–N	S–C–N	Cu–N–C	Cu–S–C
Thiocyanate co-ordinating through N				
1.61	1.17	178.3	173.8 [a]	
1.61	1.16	177.8	163.1 [b]	
1.62	1.14	177.8	167.4	
1.62	1.15	179.0	168.1 [c]	
1.63	1.14	178.4	169.6	
1.612	1.142	177.4	163.3 [d]	
1.59	1.16	177.2	154.8 [e]	
1.62	1.15	179.6	152.4 [f]	
Bridging thiocyanate				
1.633	1.152	178.2	169.0	98.3 [g]
1.62	1.16	177.7	164.9	95.1 [h]
1.63	1.15	166.2	177.2	94.3 [i]
1.63	1.16	178.9	166.4	89.4 [f]
Thiocyanate co-ordinating through S				
1.65	1.16	178.0		89.5 [j]
1.611	1.165	179.1		84.0 [k]
Unco-ordinated thiocyanate				
1.64	1.15	178.1 [j]		
1.624	1.168	178.6 [d]		
1.59	1.13	178.0 [e]		

[a] Ref. 13. [b] Ref. 17. [c] M. Cannas, G. Carta, A. Cristini, and G. Marongiu, *J.C.S. Dalton*, 1974, 1278. [d] Ref. 12. [e] Present work (I). [f] Present work (II). [g] P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, and G. Predieri, *J.C.S. Dalton*, 1975, 2357. [h] M. Cannas, G. Carta, and G. Marongiu, *J.C.S. Dalton*, 1974, 556. [i] M. Cannas, G. Carta, and G. Marongiu, *Gazzetta*, 1974, **104**, 581. [j] G. Marongiu, E. C. Lingafelter, and P. Paoletti, *Inorg. Chem.*, 1969, **8**, 2763. [k] G. D. Andreetti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1971, **101**, 483.

TABLE 7

Contacts <3.5 Å

(*a*) For (I)			
$N(6) \cdots C(14^{I})$	3.41(1)	$N(6) \cdots N(3^{IV})$	3.49(1)
$C(14) \cdots C(18^{II})$	3.45(2)	$C(12) \cdots N(6^{IV})$	3.39(1)
$C(3) \cdots N(5^{III})$	3.43(1)	$N(6) \cdots C(11)$	3.47(2)
$C(17) \cdots C(3^{III})$	3.38(2)		
(*b*) For (II)			
$Cu \cdots C(12^{III})$	3.27(1)	$S(1) \cdots N(3^{VII})$	3.31(1)
$N(1) \cdots C(11^{III})$	3.42(1)	$N(2) \cdots C(7^{III})$	3.46(1)
$N(2) \cdots C(8^{III})$	3.46(1)	$N(3) \cdots C(9^{III})$	3.43(1)
$N(4) \cdots N(4^{V})$	3.36(1)	$N(4) \cdots C(13^{V})$	3.25(1)
$N(5) \cdots C(12^{III})$	3.49(1)	$N(4) \cdots C(1)$	3.05(1)
$C(3) \cdots C(12^{VII})$	3.43(1)	$C(13) \cdots C(11^{VII})$	3.41(1)
$C(6) \cdots C(9^{III})$	3.34(1)	$C(5) \cdots C(10^{III})$	3.34(1)
$C(8) \cdots C(8^{III})$	3.36(1)	$C(6) \cdots C(10^{III})$	3.44(1)
$C(9) \cdots C(3^{VI})$	3.39(1)	$C(14) \cdots C(2^{VII})$	3.49(1)
$Cu \cdots C(11^{III})$	3.38(1)		

Roman numeral superscripts denote the following equivalent positions:

I $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$
II $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
III $1 - x, \bar{y}, \bar{z}$
IV $\bar{x}, 1 - y, \bar{z}$
V $\bar{x}, \bar{y}, \bar{z}$
VI $x, y, z - 1$
VII $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$

The thiocyanate vibrational frequencies (cm^{-1}) in both complexes are consistent with the structures determined by *X*-ray diffraction: ν(CN) 2 080vs, ν(CS) 820m, δ(NCS) 470w for co-ordinated and ν(CN) 2 050vs, ν(CS) 740w for ionic thiocyanate groups in (I); ν(CN) 2 120s, ν(CS) 705w for bridging, and ν(CN) 2 060s, ν(CS) 820w, δ(NCS) 470w for terminal thiocyanate groups in (II).

In (II) the axial interactions involving copper, already described, link the molecules in ribbons along [010] (Figure 4); packing is influenced by S(1) · · · H–N(3) (3.31 Å) hydrogen bonds and by the usual van der Waals contacts. Contacts $<$ 3.50 Å are listed in Table 7 for both complexes.

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