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[2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl-κN^2)pyridine-κN]bis(thiocyanato-*N*)copper(II)

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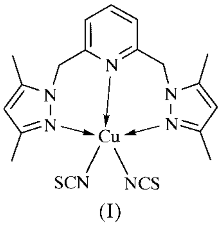
The title compound, $[Cu(NCS)_2(C_{17}H_{21}N_5)]$, displays a distorted square-pyramidal coordination geometry, where the basal plane is defined by the tridentate ligand and by one of the thiocyanate ions. The apical position is occupied by the other thiocyanate ion.

Comment

The spectroscopic and chemical properties of copper compounds of pyrazole and its derivatives have been studied intensively during the last two decades (Sheu *et al.*, 1995; Martens *et al.*, 1995; Kitajima *et al.*, 1992; Sorrell *et al.*, 1991) because of their ease of handling and manipulation in making model compounds for biological systems such as hæmocyanin and tyrosinase (Solomon *et al.*, 1992). To give more insight into the coordination behaviour of pyrazole-based ligands with copper(I) and copper(II) ions, a systematic study has been embarked on in our group (Manikandan *et al.*, 1996, 1998) of the ligand 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, *L*, containing one pyridine and two pyrazole donors. We report herein the crystal structure of (I), a monomeric copper(II) complex with the ligand *L* and two thiocyanate counter-ions.



(I)

The structure of (I) (Fig. 1) consists of a pentacoordinated Cu^{2+} ion in a distorted square-pyramidal geometry, with the three N atoms from the ligand and an N from one of the thiocyanate groups occupying the basal plane. The axial position is occupied by the second thiocyanate N atom. The axial Cu—NCS bond distance is slightly longer (by *ca* 0.16 Å) than the corresponding equatorial bond (Table 1). The Cu^{2+} ion is displaced 0.308 Å above the plane formed by N1/N2/N3/N7. The significant deviation of the basal plane is evident also from the angles N1—Cu—N2 and N3—Cu—N7, with values of 169.02 (10) and 153.71 (13)°, respectively. The pyridine and pyrazole rings are planar. The geometries of the two linear thiocyanate ligands are similar, but they differ notably in the angles they make to the Cu atom [177.7 (4) and 153.4 (3)°]. This dissimilarity destroys the approximate twofold rotational symmetry of the compound.

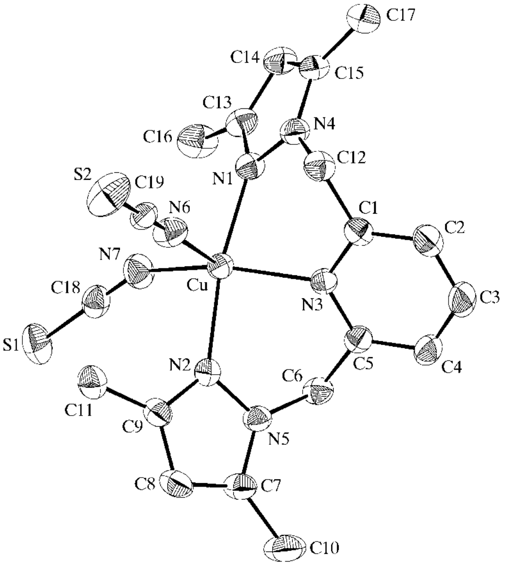


Figure 1
The molecular structure of (I), showing 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

In order to quantify the distortion of the coordination polyhedron in (I), we have calculated the dihedral angles between the polyhedral faces, and thus the parameters Δ and τ, by following the methods described by Meutterties & Guggenberger (1974) and Addison *et al.* (1984). The parameters Δ and τ describe the deviation from trigonal-bipyramidal geometry and trigonality, respectively. For the regular square-pyramid structure, the trigonality parameter τ will be zero and it increases to 1.0 as the trigonal-bipyramidal distortion increases. Similarly, Δ is zero for trigonal-bipyramidal compounds and increases to 1.0 for square-pyramidal geometry. The calculated Δ and τ values for (I) are 0.706 and 0.256, respectively, indicating more trigonal distortion from ideal square-pyramidal geometry.

Experimental

2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (*L*) was prepared using the procedure of Manikandan *et al.* (1996). To a solution of *L* (0.295 g) in methanol (30 ml) was added $Cu(ClO_4)_2{\cdot}6H_2O$ (0.37 g) followed by NH_4NCS (0.076 g) with vigorous stirring. A green precipitate was formed. The mixture was allowed to stir for a further 1 h to ensure complete conversion and was then filtered. The residue

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was washed with cold methanol/water mixture (1:1) and recrystallized from acetonitrile. Analysis found: C 47.75, H 4.55, N 20.50%; $C_{19}H_{21}N_7S_2Cu$ requires: C 48.03, H 4.46, N 20.64%.

Crystal data

$[Cu(NCS)_2(C_{17}H_{21}N_5)]$
$M_r = 475.09$
Monoclinic, $P2_1/n$
$a = 11.382$ (5) Å
$b = 12.162$ (4) Å
$c = 15.855$ (7) Å
$\beta = 103.31$ (3)°
$V = 2135.8$ (14) Å^3
$Z = 4$

$D_x = 1.478$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–15°
$\mu = 3.435$ mm^{-1}
$T = 293$ (2) K
Prism, dark green
0.32 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.337$, $T_{\rm max} = 0.503$
3237 measured reflections
3057 independent reflections
2649 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 59.91$°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.135$
$S = 1.035$
3057 reflections
267 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 1.3220P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.561$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.519$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0017 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—N7	1.974 (3)	Cu—N3	2.071 (3)
Cu—N1	2.038 (3)	Cu—N6	2.131 (3)
Cu—N2	2.041 (3)		
N7—Cu—N1	96.27 (12)	N7—Cu—N6	99.78 (14)
N7—Cu—N2	87.54 (12)	N1—Cu—N6	93.28 (11)
N1—Cu—N2	169.02 (10)	N2—Cu—N6	96.22 (11)
N7—Cu—N3	153.71 (13)	N3—Cu—N6	106.31 (12)
N1—Cu—N3	85.59 (10)	N7—C18—S1	179.1 (4)
N2—Cu—N3	86.47 (10)	N6—C19—S2	178.2 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP for PC* (Zsolnai & Pritzkow, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1259). Services for accessing these data are described at the back of the journal.

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