All programs used were those provided by *Crystal Logic* (Strouse, 1991) and all calculations were performed on a DEC 3100 computer. A 1 ml filter was used in the data collection. Standard deviations were calculated from counting statistics and included an instability factor of 0.04. Patterson and Fourier techniques were used to locate all atoms. Full-matrix isotropic refinement produced $R(F) = 0.097$ and $wR(F) = 0.126$. Anisotropic refinement of non-H atoms produced $R(F) = 0.057$ and $wR(F) = 0.082$. Theoretical H-atom positions (C—H = 0.95 Å) and absorption corrections from average pathlength calculations were included in the final cycles of refinement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, complete geometry and a view of the unit cell have been deposited with the IUCr (Reference: CR1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Isothiocyanatobis(1,10-phenanthroline)-copper(II) Perchlorate, $[\mathrm{Cu(NCS)(phen)_2}]\mathrm{ClO_4}$

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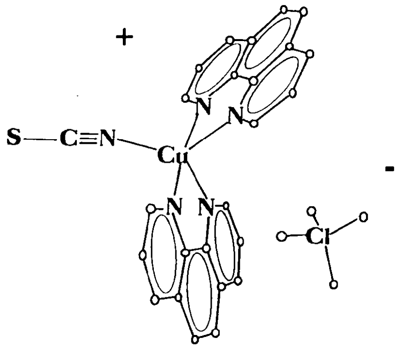
Abstract

The crystal structure of $[\mathrm{Cu(NCS)(C_{12}H_8N_2)_2}]\mathrm{ClO_4}$, containing a five-coordinate copper(II) atom with a distorted trigonal-bipyramidal $[\mathrm{Cu^{II}N_5}]$ core, is reported. The Cu—NCS distance is 2.005 (5) Å with Cu bonded to the N-atom end of the isothiocyanate, while the Cu—N distances to the 1,10-phenanthrolines average 2.069 (4) Å for the equatorial positions and 2.002 (4) Å for the axial positions. The geometry is distorted from trigonal bipyramidal stereochemistry because the N—Cu—N angles of the 1,10-phenanthrolines average only 80.5 (2)°. The axial N and Cu atoms are almost linear with an angle of 174.8 (2)°. The isothiocyanate chain is approximately linear [178.7 (5)°] and bent at 166.1 (5)° from the Cu atom. This is the first report of a five-coordinate copper(II) complex containing a nitrogen-bonded thiocyanate ligand.

Comment

The stereochemistry of five-coordinate copper(II) shows molecular conformations ranging from a slightly distorted trigonal-bipyramidal (Greiner, Breneman, Parker & Willett, 1994) to a distorted square-pyramidal arrangement (Hathaway & Murphy, 1980; Harrison, Kennedy, Power, Sheahan & Hathaway, 1981). The determination of the molecular and crystal structure of $[\mathrm{Cu(NCS)(phen)_2}]\mathrm{ClO_4}$, (I), was initiated in order to study the bond and angle distortions displayed by five-coordinate copper(II) when one of the ligands is a bulky isothiocyanate group.



(I)

An *ORTEP* (Johnson, 1965) plot of the complex with the H atoms omitted and the numbering system indicated is shown in Fig. 1. The packing of the complex in a unit cell is shown as a stereoscopic plot in Fig. 2.

The average Cu—N(phen) distances of 2.069 (4) Å for equatorial and 2.002 (4) Å for axial positions are comparable to those reported for $[\mathrm{Cu(CN)(phen)_2}]\mathrm{NO_3.H_2O}$ [2.112 (10) and 2.000 (10) Å, respectively (Anderson, 1975)], $[\mathrm{CuCl(phen)_2}]\mathrm{ClO_4}$ [2.107 (6) and 1.995 (6) Å, respectively (Boys, Escobar & Martínez-Carrera, 1981)], $[\mathrm{CuCl(phen)_2}]\mathrm{NO_3.H_2O}$ [2.112 (4) and 1.989 (4) Å, respectively (Boys, 1988)] and $[\mathrm{CuBr(phen)_2}]\mathrm{ClO_4}$ [2.091 (3) and 1.985 (5) Å, respectively (Greiner, Breneman, Parker & Willett, 1994)]. The Cu—N(NCS) distance is 2.005 (4) Å with Cu bonded to the N-atom end of the isothiocyanate chain, with a slight bend for Cu—N1—C1 [166.1 (5)°]. The isothiocyanate moiety is very nearly linear [178.7 (5)°]. The N1—C1 and S—C1 distances [1.138 (6) and 1.629 (6) Å, respectively] of the isothiocyanate are virtually identical

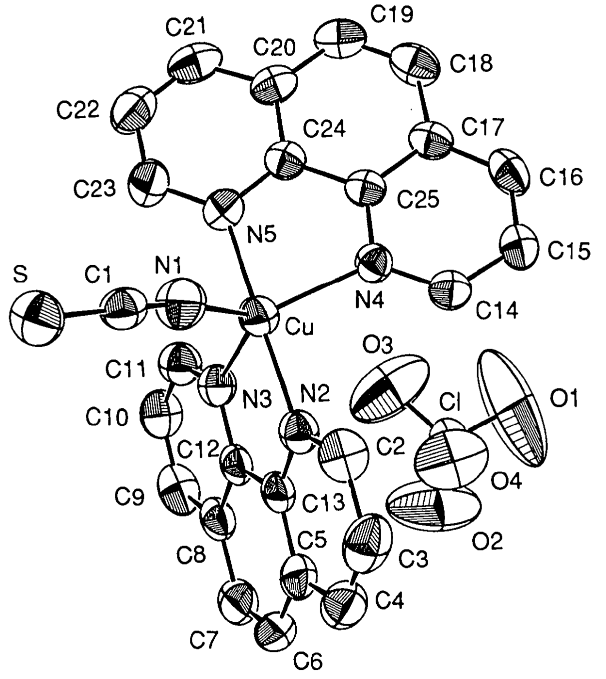


Fig. 1. *ORTEP* (Johnson, 1965) plot of $[Cu(NCS)(phen)_2]ClO_4$ showing the atom-numbering scheme. H atoms have been omitted. Displacement ellipsoids are plotted at the 50% probability level.

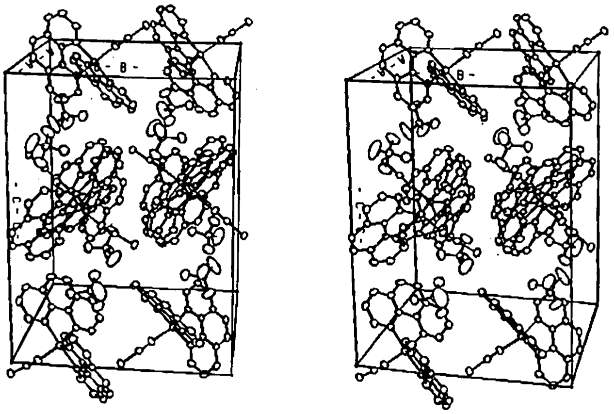


Fig. 2. Stereoscopic plot of the unit cell for $[Cu(NCS)(phen)_2]ClO_4$.

to those reported for $Cu(phen)(NCS)_2$ [1.148 (6) and 1.628 (5) Å, respectively (Breneman & Parker, 1993)].

The N—Cu—N angles of the 1,10-phenanthrolines are 80.4 (2) and 80.6 (2)°, which are very close to the angles [80.5 (3)–81.7 (2)°] reported for all the complexes referenced in the previous paragraph. The near-linear nature [174.8 (2)°] of the axial N atoms and Cu center in the title compound is consistent with the angles reported previously. This almost linear angle varies from 174.3 (3) to 177.0 (3)° in the other complexes.

The equatorial angles in $[Cu(NCS)(phen)_2]ClO_4$ are: N3(phen)—Cu—N4(phen) 116.1 (1), N4(phen)—Cu—N1(NCS) 125.9 (2) and N1(NCS)—Cu—N3(phen) 118.0 (2)°. These angles vary, ranging from those in $[CuBr(phen)_2]ClO_4$ (Greiner, Breneman, Parker & Willett, 1994), which are nearly equal at 120.0 (2)°, to those in $[Cu(CN)(phen)_2]NO_3.H_2O$ (Anderson, 1975), which are as large as 129.0 (3) and 132.4 (3)° between the cyanide and the equatorial N atoms from two different phenanthrolines. In the latter complex the equatorial angle between the two different phenanthrolines was pinched to 98.6 (2)°.

The perchlorate ion is somewhat disordered. A model involving three overlapping fractional ions based on peaks found in the difference fourier map did not result in a lower *R* value than one using one ion with large temperature factors for the O atoms; therefore, this latter, simpler model was used. The average Cl—O bond length is 1.364 (5) Å. The average O—Cl—O angle is 109.4 (4)°. These values compare well with those values found for the ordered perchlorate ion of $[CuBr(phen)_2]ClO_4$ [1.384 (5) Å and 109.6 (5)°, respectively (Greiner, Breneman, Parker & Willett, 1994)].

Experimental

The compound $[Cu(NCS)(phen)_2]ClO_4$ was prepared by the slow addition of a 20 ml solution of 1,10-phenanthroline monohydrate (1.98 g, 10.0 mmol) in ethanol to a 25 ml solution of $Cu(ClO_4)_2.6H_2O$ (1.85 g, 5.0 mmol) dissolved in water. To the resulting solution, which contained a yellow-green precipitate, solid NH_4SCN (0.38 g, 5.0 mmol) was added slowly with continuous stirring. The product, a mustard-green solid, was washed with a small volume of ethanol and anhydrous ether. The light green solid was dissolved in DMSO and a single crop of bright green crystals was produced by evaporation of the solvent.

Crystal data

$[Cu(NCS)(C_{12}H_8N_2)_2]ClO_4$
$M_r = 581.49$
Orthorhombic
Pbca
$a = 14.737\ (2)$ Å
$b = 15.200\ (1)$ Å
$c = 20.762\ (3)$ Å
$V = 4651\ (1)$ Å^3
$Z = 8$
$D_x = 1.66$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$17.4°$
$\mu = 1.186$ mm^{-1}
$T = 293$ K
Prism
0.50 × 0.20 × 0.13 mm
Light green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.920$, $T_{max} = 0.999$
3611 measured reflections
3611 independent reflections
2270 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 22$
1 standard reflection
frequency: 167 min
intensity variation: 0.82%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.047$
$S = 1.77$
2270 reflections
398 parameters
All H-atom parameters refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Atomic scattering factors from *MolEN* (Fair, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.11111 (4)	0.29710 (3)	0.46641 (3)	0.0451 (1)
Cl	0.12065 (8)	0.15163 (8)	0.26239 (6)	0.0553 (4)
S	0.1596 (1)	0.54533 (8)	0.59980 (7)	0.0598 (4)
O1	0.0547 (4)	0.1045 (4)	0.2407 (4)	0.260 (3)
O2	0.1969 (3)	0.1475 (4)	0.2249 (3)	0.162 (3)
O3	0.1428 (5)	0.1222 (4)	0.3234 (3)	0.165 (3)
O4	0.0931 (3)	0.2404 (3)	0.2686 (2)	0.109 (1)
N1	0.1118 (3)	0.4017 (3)	0.5253 (2)	0.063 (1)
N2	0.1362 (2)	0.3717 (2)	0.3891 (2)	0.043 (1)
N3	0.2374 (2)	0.2435 (2)	0.4382 (2)	0.0424 (9)
N4	−0.0041 (2)	0.2332 (2)	0.4311 (2)	0.0393 (9)
N5	0.0893 (2)	0.2129 (2)	0.5391 (2)	0.048 (1)
C1	0.1306 (3)	0.4606 (3)	0.5564 (2)	0.046 (1)
C2	0.0845 (3)	0.4360 (3)	0.3655 (3)	0.058 (1)
C3	0.1110 (4)	0.4843 (3)	0.3122 (3)	0.067 (1)
C4	0.1909 (4)	0.4688 (3)	0.2827 (2)	0.063 (1)
C5	0.2469 (3)	0.4006 (3)	0.3057 (2)	0.049 (1)
C6	0.3315 (4)	0.3761 (3)	0.2770 (2)	0.063 (1)
C7	0.3813 (3)	0.3089 (3)	0.3001 (2)	0.061 (1)
C8	0.3515 (3)	0.2607 (3)	0.3555 (2)	0.048 (1)
C9	0.4016 (3)	0.1920 (3)	0.3840 (3)	0.062 (1)
C10	0.3690 (3)	0.1513 (3)	0.4374 (3)	0.060 (1)
C11	0.2871 (3)	0.1787 (3)	0.4626 (2)	0.054 (1)
C12	0.2695 (3)	0.2838 (3)	0.3849 (2)	0.042 (1)
C13	0.2162 (3)	0.3544 (3)	0.3593 (2)	0.040 (1)
C14	−0.0503 (3)	0.2440 (3)	0.3775 (2)	0.045 (1)
C15	−0.1247 (3)	0.1932 (3)	0.3606 (2)	0.052 (1)
C16	−0.1528 (3)	0.1290 (3)	0.4011 (2)	0.053 (1)
C17	−0.1065 (3)	0.1140 (3)	0.4593 (2)	0.043 (1)
C18	−0.1302 (3)	0.0490 (3)	0.5058 (3)	0.054 (1)
C19	−0.0824 (3)	0.0385 (3)	0.5611 (2)	0.053 (1)
C20	−0.0062 (3)	0.0917 (3)	0.5744 (2)	0.046 (1)
C21	0.0474 (4)	0.0874 (3)	0.6303 (2)	0.059 (1)
C22	0.1165 (4)	0.1434 (3)	0.6399 (2)	0.062 (1)
C23	0.1356 (3)	0.2060 (3)	0.5938 (2)	0.058 (1)
C24	0.0190 (3)	0.1574 (3)	0.5300 (2)	0.040 (1)
C25	−0.0319 (3)	0.1680 (3)	0.4720 (2)	0.037 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu—N1	2.005 (5)	C5—C6	1.431 (8)
Cu—N2	1.999 (4)	C5—C13	1.391 (6)
Cu—N3	2.113 (4)	C6—C7	1.347 (8)
Cu—N4	2.089 (4)	C7—C8	1.433 (7)
Cu—N5	2.004 (4)	C8—C9	1.409 (8)
Cl—O1	1.289 (6)	C8—C12	1.400 (6)
Cl—O2	1.368 (5)	C9—C10	1.358 (8)
Cl—O3	1.382 (6)	C10—C11	1.381 (8)
Cl—O4	1.416 (5)	C12—C13	1.431 (6)
S—C1	1.629 (6)	C14—C15	1.386 (7)
N1—C1	1.138 (6)	C15—C16	1.353 (7)
N2—C2	1.332 (6)	C16—C17	1.407 (7)
N2—C13	1.358 (6)	C17—C18	1.426 (7)
N3—C11	1.329 (6)	C17—C25	1.397 (6)
N3—C12	1.351 (5)	C18—C19	1.356 (8)
N4—C14	1.315 (6)	C19—C20	1.411 (7)
N4—C25	1.368 (5)	C20—C21	1.406 (7)
N5—C23	1.329 (6)	C20—C24	1.409 (6)
N5—C24	1.350 (6)	C21—C22	1.342 (8)
C2—C3	1.386 (8)	C22—C23	1.379 (8)
C3—C4	1.348 (9)	C24—C25	1.428 (6)
C4—C5	1.408 (8)		
N1—Cu—N2	92.2 (2)	Cu—N3—C12	111.1 (3)
N1—Cu—N3	118.0 (2)	C11—N3—C12	117.1 (4)
N1—Cu—N4	125.9 (2)	Cu—N4—C14	131.3 (3)
N1—Cu—N5	92.8 (2)	Cu—N4—C25	111.3 (3)
N2—Cu—N3	80.4 (2)	C14—N4—C25	117.4 (4)
N2—Cu—N4	97.6 (1)	Cu—N5—C23	127.7 (4)
N2—Cu—N5	174.8 (2)	Cu—N5—C24	114.7 (3)
N3—Cu—N4	116.1 (1)	C23—N5—C24	117.7 (4)
N3—Cu—N5	95.9 (2)	S—C1—N1	178.7 (5)
N4—Cu—N5	80.6 (2)	N2—C2—C3	121.5 (6)
O1—Cl—O2	113.2 (6)	C2—C3—C4	121.1 (6)
O1—Cl—O3	108.6 (6)	C3—C4—C5	119.1 (6)
O1—Cl—O4	110.2 (5)	C4—C5—C6	124.1 (5)
O2—Cl—O3	108.2 (4)	C4—C5—C13	116.9 (5)
O2—Cl—O4	109.3 (3)	C6—C5—C13	119.0 (5)
O3—Cl—O4	107.0 (4)	C5—C6—C7	121.6 (6)
Cu—N1—C1	166.1 (5)	C6—C7—C8	120.4 (6)
Cu—N2—C2	127.3 (4)	C7—C8—C9	123.7 (5)
Cu—N2—C13	114.6 (3)	C7—C8—C12	119.2 (5)
C2—N2—C13	118.1 (4)	C9—C8—C12	117.1 (5)
C9—C10—C11	118.8 (6)	C8—C9—C10	119.7 (6)
N3—C11—C10	124.2 (6)	C17—C18—C19	121.9 (5)
N3—C12—C8	123.2 (4)	C18—C19—C20	120.8 (5)
N3—C12—C13	116.9 (4)	C19—C20—C21	125.6 (5)
C8—C12—C13	119.9 (4)	C19—C20—C24	119.2 (5)
N2—C13—C5	123.3 (4)	C21—C20—C24	115.2 (5)
N2—C13—C12	116.8 (4)	C20—C21—C22	121.3 (6)
C5—C13—C12	119.9 (4)	C21—C22—C23	119.4 (6)
N4—C14—C15	123.6 (5)	N5—C23—C22	122.8 (6)
C14—C15—C16	119.1 (5)	N5—C24—C20	123.7 (4)
C15—C16—C17	120.2 (5)	N5—C24—C25	116.8 (4)
C16—C17—C18	125.2 (5)	C20—C24—C25	119.6 (4)
C16—C17—C25	116.6 (4)	N4—C25—C17	123.0 (4)
C18—C17—C25	118.2 (5)	N4—C25—C24	116.6 (4)
Cu—N3—C11	131.8 (4)	C17—C25—C24	120.4 (4)

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: ST1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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