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cis-Chloro(isothiocyanato)bis(1,10-phenanthroline)copper(II), *cis*-[CuCl(NCS)(phen)$_2$]

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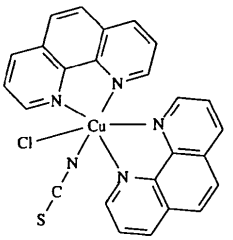
Abstract

The crystal structure of green [CuCl(NCS)(C$_{12}$H$_8$N$_2$)$_2$], containing six-coordinate copper(II) with a tetragonal [Cu^{II}N$_5$Cl] core, is reported. The copper to isothiocyanate distance is 1.960 (6) Å, with Cu bonded to the N-atom end of the thiocyanate moiety. The three remaining short distances for the tetragonal core are Cu—N distances to the 1,10-phenanthrolines which are 2.043 (5), 2.060 (4) and 2.064 (4) Å. One of the long distances to the Cu-atom center is occupied by an N atom of a 1,10-phenanthroline with a Cu—N distance of 2.370 (5) Å, and the other long interaction has a Cu—Cl distance of 2.679 (2) Å.

Comment

Several five-coordinate complexes of Cu^{II} have been synthesized with one of the two potentially single-charged negative ions residing in the coordination sphere of copper and the other singly charged anion occupying a position outside the copper coordination sphere. In most cases the anion occupying the position external to the coordination sphere is a ligand such as perchlorate which has a low tendency to coordinate. The isothiocyanato complex [Cu(NCS)(phen)$_2$]ClO$_4$, where phen = 1,10-phenanthroline, has been synthesized and its structure determined (Parker, Manson & Breneman, 1994). The five-coordinate copper(II) complex [Cu(bipy)$_2$I]I (bipy = 2,2′-bipyridine) (Barclay & Kennard, 1961), has a potential ligand, I$^-$, as an anion external to the coordination sphere of the Cu atom. A structural determination of [Cu(bipy)$_2$Cl]Cl.6H$_2$O (Stephens & Tucker, 1973) revealed five-coordinate copper(II) with an external Cl$^-$ ion. This work indicates that other five-coordinate copper(II) complexes might be synthesized with a free Cl$^-$ anion. This paper reports the results of an attempt to use thiocyanate as the coordinating ligand and Cl$^-$ as a counterion. The synthesis and structural determination of [CuCl(NCS)(phen)$_2$], (I), showed it to be a six-coordinate copper(II) complex. Preliminary work with the analogous bromide complex [CuBr(NCS)(phen)$_2$] (Parker & Breneman, 1994) shows that it is also six-coordinate.



(I)

The stereochemistry of the five-coordinate complex [Cu(NCS)(phen)$_2$]ClO$_4$ (Parker, Manson, & Breneman, 1994) has an N-atom-bonded thiocyanate as the stem of an inverted umbrella formed by the two 1,10-phenanthroline ligands. On the reverse side of the thiocyanate ligand, the perchlorate anion snuggles in the void formed by the two 1,10-phenanthroline ligands. The perchlorate anion is slightly displaced in [Cu(NCS)(phen)$_2$]ClO$_4$ unlike the perchorate anion in [CuBr(phen)$_2$]ClO$_4$ (Greiner, Breneman, Parker & Willett, 1994), which occupies a similar position on the twofold axis parallel to the *b* axis on which the atoms Cl, Cu and Br reside. In contrast to the two previous compounds, the chloride ion in the six-coordinate complex [CuCl(NCS)(phen)$_2$] resides in the coordination sphere of the Cu atom and is *cis* to the thiocyanate ligand. The Cl$^-$ ion occupies one of the two long-bonding positions. An *ORTEP* (Johnson, 1965) plot of the complex is shown in Fig. 1 with the atom-numbering system. The packing of the complex in a unit cell is shown as a stereoscopic plot in Fig. 2.

The long distance of one of the 1,10-phenanthroline N atoms from the metal center is in contrast to the Cu—N distances in the two previously mentioned five-coordinate complexes, all of which are almost equal. The short Cu—N(phen) distances of 2.043 (5)–2.064 (4) Å for the equatorial and 2.370 (5) Å for the axial position are comparable to those reported for [Cu(phen)$_3$](ClO$_4$)$_2$ [2.00 (1)–2.06 (1) Å for the equatorial and 2.32 (1)–2.34 (1) Å for the axial (Anderson, 1973)], [Cu(PF$_6$)(Him)(phen)$_2$] (Him = imidazole) [2.008 (6)–2.042(5) for the equatorial and 2.219 (7) Å for the axial (Mikuriya, Kushida, Okawa & Oshio, 1989)], and [Cu(bipy)$_3$](ClO$_4$)$_2$ [2.026 (5)–2.036 (5) Å for the equatorial and 2.226 (7)–2.450 (7) Å for the axial (Anderson, 1972)]. The Cu—N(NCS) distance is 1.960 (6) Å with

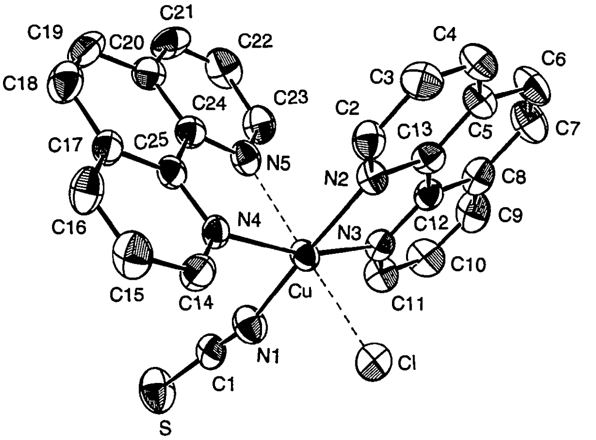


Fig. 1. *ORTEP* (Johnson, 1965) plot of [CuCl(NCS)(phen)$_2$] showing the atom-numbering scheme. The H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.

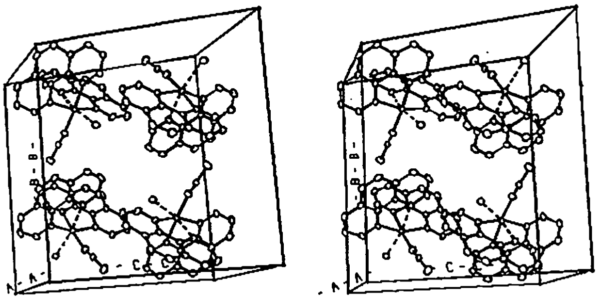


Fig. 2. Stereoscopic plot of the unit cell of [CuCl(NCS)(phen)$_2$].

the Cu bonded to the N-atom end of the thiocyanate ion with a slight bend of 165.2 (5)° along Cu—N1—C1.

The N—Cu—N chelate angle of the 1,10-phenanthroline with short bonding distances is 80.6 (2)°, which is very close to the range of angles [80.4 (3)–81.9 (2)°] reported for the tetragonal six-coordinate complexes referenced in the previous paragraph. The N—Cu—N angle of the 1,10-phenanthroline with the one long bonding distance is 75.6 (2)°, which compares well with the range [72.2 (5)–79.1 (3)°] for the previously referenced complexes.

The N1—Cu—N2 bond angle is 174.5 (2)°, whereas the N3—Cu—N4 angle is 162.2 (2)°. This distortion may be the result of the coordination of the 1,10-phenanthroline which has two N atoms bonded to the Cu-atom center at short distances. The Cl—Cu—N5 bond angle is 169.9 (1)°. The thiocyanate ion is close to linear with an angle of 178.6 (6)°. The thiocyanate ligand is displaced away from the Cl^- ligand with a bonding angle Cu—N—C of 165.2 (5)°.

Experimental

The compound [CuCl(NCS)(phen)$_2$] was prepared by the slow addition of a 25 ml solution of 1,10-phenanthroline monohydrate (3.96 g, 20.0 mmol) in ethanol to a 15 ml solution of $CuCl_2.2H_2O$ (1.71 g, 10.0 mmol) dissolved in water. To the resulting solution, which contained a yellow-green precipitate, solid NH_4SCN (0.76 g, 10.0 mmol) was slowly added with continuous stirring. The product was a lime-green solid which 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

[CuCl(NCS)($C_{12}H_8N_2$)$_2$]
$M_r = 517.50$
Monoclinic
$P2_1/c$
$a = 10.828$ (6) Å
$b = 16.339$ (3) Å
$c = 15.034$ (6) Å
$\beta = 125.50$ (2)°
$V = 2165$ (2) Å^3
$Z = 4$
$D_x = 1.59$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–17.5°
$\mu = 1.25$ mm^{-1}
$T = 293$ K
Square prism
0.20 × 0.20 × 0.10 mm
Light green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.928$, $T_{\max} = 0.998$
3973 measured reflections
3605 independent reflections

2048 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.02$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 17$
1 standard reflection
frequency: 167 min
intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.046$
$S = 1.26$
2048 reflections
362 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968)

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	0.31806 (6)	−0.24277 (4)	−0.26375 (5)	0.0314 (1)
Cl	0.1924 (1)	−0.14544 (9)	−0.1933 (1)	0.0412 (4)
S	0.5550 (2)	−0.0544 (1)	−0.3551 (1)	0.0591 (6)
N1	0.3956 (4)	−0.1527 (3)	−0.3044 (3)	0.044 (1)
N2	0.2210 (4)	−0.3379 (3)	−0.2369 (3)	0.030 (1)
N3	0.1308 (4)	−0.2617 (3)	−0.4214 (3)	0.032 (1)
N4	0.5235 (4)	−0.2587 (3)	−0.1142 (3)	0.030 (1)
N5	0.4464 (4)	−0.3418 (3)	−0.2973 (3)	0.034 (1)
C1	0.4611 (5)	−0.1131 (3)	−0.3259 (4)	0.034 (1)
C2	0.2652 (5)	−0.3739 (4)	−0.1437 (4)	0.038 (1)
C3	0.1892 (6)	−0.4402 (4)	−0.1397 (4)	0.042 (2)
C4	0.0640 (5)	−0.4705 (4)	−0.2324 (4)	0.046 (3)
C5	0.0144 (5)	−0.4344 (4)	−0.3318 (4)	0.039 (1)
C6	−0.1168 (6)	−0.4617 (4)	−0.4364 (4)	0.052 (3)

C7	−0.1600 (6)	−0.4251 (4)	−0.5297 (4)	0.054 (3)
C8	−0.0781 (5)	−0.3560 (4)	−0.5293 (4)	0.039 (1)
C9	−0.1136 (6)	−0.3142 (4)	−0.6227 (4)	0.052 (3)
C10	−0.0289 (6)	−0.2493 (4)	−0.6143 (4)	0.047 (3)
C11	0.0911 (6)	−0.2245 (4)	−0.5114 (4)	0.039 (1)
C12	0.0486 (5)	−0.3274 (3)	−0.4297 (4)	0.032 (1)
C13	0.0935 (5)	−0.3669 (3)	−0.3302 (4)	0.032 (1)
C14	0.5635 (5)	−0.2169 (4)	−0.0262 (4)	0.042 (2)
C15	0.6988 (6)	−0.2295 (4)	0.0755 (4)	0.049 (3)
C16	0.7962 (6)	−0.2875 (4)	0.0863 (4)	0.046 (3)
C17	0.7597 (5)	−0.3326 (3)	−0.0039 (4)	0.033 (1)
C18	0.8554 (6)	−0.3953 (4)	−0.0002 (4)	0.048 (3)
C19	0.8171 (6)	−0.4367 (4)	−0.0891 (4)	0.049 (3)
C20	0.6771 (5)	−0.4218 (3)	−0.1941 (4)	0.038 (1)
C21	0.6282 (5)	−0.4640 (4)	−0.2902 (4)	0.047 (1)
C22	0.4967 (6)	−0.4452 (4)	−0.3831 (4)	0.052 (3)
C23	0.4087 (6)	−0.3825 (4)	−0.3852 (4)	0.043 (2)
C24	0.5794 (5)	−0.3617 (3)	−0.2025 (4)	0.032 (1)
C25	0.6210 (5)	−0.3157 (3)	−0.1041 (4)	0.030 (1)

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

Cu—Cl	2.679 (2)	C5—C13	1.389 (8)
Cu—N1	1.960 (6)	C6—C7	1.33 (1)
Cu—N2	2.043 (5)	C7—C8	1.434 (9)
Cu—N3	2.060 (4)	C8—C9	1.399 (9)
Cu—N4	2.064 (4)	C8—C12	1.399 (8)
Cu—N5	2.370 (5)	C9—C10	1.36 (1)
S—C1	1.633 (7)	C10—C11	1.382 (9)
N1—C1	1.137 (7)	C12—C13	1.430 (8)
N2—C2	1.326 (8)	C14—C15	1.388 (9)
N2—C13	1.360 (7)	C15—C16	1.36 (1)
N3—C11	1.308 (8)	C16—C17	1.384 (9)
N3—C12	1.353 (7)	C17—C18	1.435 (9)
N4—C14	1.319 (8)	C17—C25	1.405 (8)
N4—C25	1.349 (7)	C18—C19	1.33 (1)
N5—C23	1.315 (8)	C19—C20	1.438 (9)
N5—C24	1.352 (7)	C20—C21	1.40 (1)
C2—C3	1.383 (9)	C20—C24	1.396 (8)
C3—C4	1.353 (9)	C21—C22	1.33 (1)
C4—C5	1.392 (9)	C22—C23	1.39 (1)
C5—C6	1.448 (9)	C24—C25	1.476 (8)

Cl—Cu—N1	94.9 (2)	C19—C20—C24	118.6 (7)
Cl—Cu—N2	86.3 (1)	C21—C20—C24	116.2 (6)
Cl—Cu—N3	99.0 (1)	C20—C21—C22	120.3 (7)
Cl—Cu—N4	96.8 (1)	C21—C22—C23	119.9 (8)
Cl—Cu—N5	169.9 (1)	C4—C5—C13	117.9 (6)
N1—Cu—N2	174.5 (2)	C6—C5—C13	118.0 (6)
N1—Cu—N3	93.9 (2)	C5—C6—C7	121.8 (7)
N1—Cu—N4	92.8 (2)	C6—C7—C8	120.7 (7)
N2—Cu—N3	80.6 (2)	C7—C8—C9	124.8 (7)
N2—Cu—N4	92.4 (2)	C7—C8—C12	119.1 (6)
N3—Cu—N4	162.2 (2)	C9—C8—C12	116.1 (6)
N1—Cu—N5	92.1 (2)	C8—C9—C10	120.6 (7)
N2—Cu—N5	87.4 (2)	C9—C10—C11	118.6 (7)
N3—Cu—N5	87.7 (2)	N3—C11—C10	123.5 (7)
N4—Cu—N5	75.6 (2)	N3—C12—C8	123.1 (6)
Cu—N1—C1	165.2 (5)	N3—C12—C13	117.1 (5)
Cu—N2—C2	129.4 (4)	C8—C12—C13	119.8 (6)
Cu—N2—C13	113.1 (4)	N2—C13—C5	122.8 (6)
C2—N2—C13	117.5 (5)	N2—C13—C12	116.5 (5)
Cu—N3—C11	129.3 (4)	C5—C13—C12	120.6 (6)
Cu—N3—C12	112.4 (4)	N4—C14—C15	123.4 (6)
C11—N3—C12	118.0 (5)	C14—C15—C16	119.1 (7)
Cu—N4—C14	123.1 (4)	C15—C16—C17	119.7 (6)
Cu—N4—C25	119.2 (4)	C16—C17—C18	123.6 (6)
C14—N4—C25	117.7 (5)	C16—C17—C25	117.8 (6)
C23—N5—C24	117.3 (6)	C18—C17—C25	118.6 (6)
S—C1—N1	178.6 (6)	N5—C23—C22	122.8 (7)
N2—C2—C3	122.4 (7)	N5—C24—C20	123.5 (6)
C2—C3—C4	120.5 (7)	N5—C24—C25	116.9 (5)
C3—C4—C5	118.8 (7)	C20—C24—C25	119.6 (6)
C4—C5—C6	124.0 (6)	N4—C25—C17	122.4 (6)
C17—C18—C19	121.8 (7)	N4—C25—C24	118.3 (5)
C18—C19—C20	122.1 (7)	C17—C25—C24	119.3 (5)
C19—C20—C21	125.2 (7)		

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction, structure solution, structure refinement, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HR1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Ethylenediamine-*N*,*N*′)(1,4,7,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)nickel(II) Diperchlorate

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Abstract

Two slightly different complex ions, related by a pseudo-twofold axis, exist in the asymmetric unit of the title compound, $[Ni(C_2H_8N_2)(C_{10}H_{24}N_4)](ClO_4)_2$. There is a mirror plane passing through the Ni and four ligand N atoms in each complex ion. The Ni^{II} ion is six-coordinate in a distorted octahedral arrangement,