O22′	0.114 (2)	0.6534 (18)	0.3793 (18)	0.150†
O23	0.0483 (6)	0.7425 (11)	0.3076 (8)	0.192 (6)
O24	0.1415 (6)	0.7435 (9)	0.2435 (8)	0.172 (5)

† Fixed U_{iso}.

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

Cu—N7	2.299 (9)	Cu—N7′	2.100 (9)
Cu—N10	1.975 (9)	Cu—N10′	1.934 (8)
Cu—N13	2.320 (9)	Cu—N13′	2.103 (8)
N7—C1	1.394 (9)	N7′—C1′	1.410 (10)
N7—C8	1.278 (12)	N7′—C8′	1.277 (12)
N10—C9	1.365 (12)	N10′—C9′	1.318 (12)
N10—C11	1.343 (11)	N10′—C11′	1.355 (12)
N13—C12	1.274 (12)	N13′—C12′	1.305 (11)
N13—C14	1.408 (11)	N13′—C14′	1.391 (9)
N7—Cu—N10	77.4 (4)	N10—Cu—N13′	97.3 (3)
N7—Cu—N13	149.4 (3)	N13—Cu—N10′	118.5 (4)
N7—Cu—N7′	86.5 (3)	N13—Cu—N7′	92.4 (3)
N7—Cu—N10′	91.4 (3)	N13—Cu—N13′	95.8 (3)
N7—Cu—N13′	97.0 (3)	N7′—Cu—N10′	79.8 (4)
N10—Cu—N13	73.4 (4)	N7′—Cu—N13′	157.0 (4)
N10—Cu—N7′	105.5 (3)	N10′—Cu—N13′	77.4 (4)
N10—Cu—N10′	167.1 (4)		

The high value for the conventional *R* factor is attributed to poor crystal quality, as indicated by preliminary oscillation and Weissenberg photography. It was particularly noticeable that relatively few reflections appeared at higher angles. Several axial and zero-layer reflections were checked intermittently as a means of detecting possible crystal movement. They gave no sign of crystal decay. Disorder in the perchlorate counteranions was originally modelled by allowing all O atoms to refine with anisotropic displacement parameters, but the extreme thermal motion observed for atoms O14 and O22 required each of these atoms to be modelled by two components and O14′ and O22′ were introduced into the model to accomplish this. All four disorder components were refined with a fixed U_{iso} of 0.15 Å^2.

Data collection: local programs. Cell refinement: local programs. Data reduction: local programs. Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

The authors thank the SERC for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1197). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Diisothiocyanatobis(1,10-phenanthroline)copper(II), [Cu(NCS)$_2$(C$_{12}$H$_8$N$_2$)$_2$]

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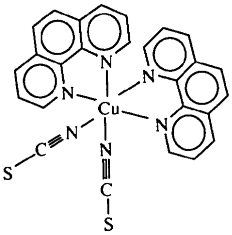
Abstract

The crystal and molecular structure of green *cis*-[Cu(NCS)$_2$(phen)$_2$] (phen = 1,10-phenanthroline) containing a distorted octahedral [Cu$^{\text{II}}$N$_6$] core is reported. The structure of [Cu(NCS)$_2$(phen)$_2$] consists of discrete molecules in which the six-coordinate Cu atom sits on a twofold rotation axis with the thiocyanates coordinating through the N atom. The Cu—N$_{\text{NCS}}$ distances are 2.020 (7) Å, while the Cu—N$_{\text{phen}}$ distances are 2.132 (5) Å *trans* to NCS and 2.217 (5) Å *trans* to N$_{\text{phen}}$. The geometry is distorted from octahedral stereochemistry because of the 76.9 (2)° N—Cu—N bite angle of each 1,10-phenanthroline and because of a slight elongation of the *trans* positions that are occupied by an N atom from each phenanthroline ligand. The thiocyanate ions are linear [N—C—S = 178.9 (6)°] and are at an angle of 161.0 (6)° to the Cu atom.

Comment

The title compound, (I), is an analog of [Fe(NCS)$_2$(phen)$_2$] and [Mn(NCS)$_2$(phen)$_2$]. The iron complex is the archetype of a series of complexes that exhibit a spin-state crossover between the high-spin ($^5T_2$) and low-spin ($^1A_1$) states (Konig & Madega, 1967; Konig, Madeja & Watson, 1968; Ganguli, Gütlich & Müller, 1981). The manganese complex has a distorted octahedral [Mn$^{\text{II}}$N$_6$] core (Holleman, Parker & Breneman, 1994). Here, we report the crystal and molecular structure of the copper complex *cis*-[Cu(NCS)$_2$(phen)$_2$], (I).



(I)

The structure of [Cu(NCSe)$_2$(phen)$_2$] shows a similar *trans* distortion and similar bond distances (Sedov, Dunaj-Jurco, Kabesova, Gazo & Garat, 1982). In this compound, the Cu—N_{NCSe} distances were found to be 2.04 Å, while the Cu—N_{phen} distances are 2.13 and 2.18 Å. The authors report that $[Cu(NCS)_2(phen)_2]$ is isomorphous (*Pbcn*, $Z = 4$) with $[Cu(NCSe)_2(phen)_2]$. With polycrystalline samples, O'Leary, Tyagi & Hathaway (1983) reported that $[Cu(NCS)_2(phen)_2]$ is isomorphous with $[Zn(NCS)_2(phen)_2]$, based on X-ray powder photographs. Hathaway also notes that being isomorphous does not mean that the MN_4N_2 chromophores are isostructural. An *ORTEP*II (Johnson, 1976) plot of the title complex with the H atoms omitted is shown in Fig. 1, along with the numbering system.

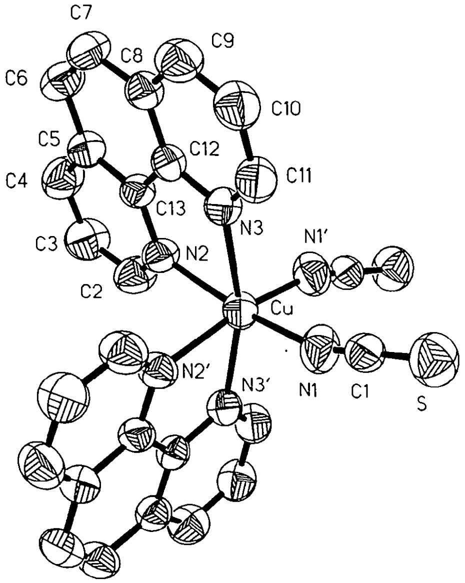


Fig. 1. Displacement ellipsoid (50% probability) plot of $[Cu(NCS)_2(phen)_2]$ showing the atom-numbering scheme. H atoms have been omitted.

The N—Cu—N bite angles of the 1,10-phenanthrolines are 76.9 (2)°. The Cu—N_{phen} distances of 2.132 (5) and 2.217 (5) Å are comparable to those of 2.13 (8) and 2.18 (8) Å in *cis*-$[Cu^{II}(NCSe)_2(phen)_2]$ (Sedov, Dunaj-Jurco, Kabesova, Gazo & Garat, 1982), with both compounds exhibiting a *trans* elongated distortion. For *cis*-$[Mn^{II}(Cl)_2(bipy)_2]$ (Lumme & Lindell, 1988), the Mn—N_{bipy} distances that are *trans* to Cl are the longer distances; the same *trans* distortion is observed in *cis*-$[Mn(NCS)_2(bipy)_2]$ (Veidis, Dockum, Charron, Reiff & Brennan, 1981). The *cis*-$[Mn(NCS)_2(phen)_2]$ complex previously reported by us shows no significant difference in the Mn—N_{phen} distances (Holleman, Parker & Breneman, 1994).

The Cu—N_{NCS} distance is 2.020 (7) Å in $[Cu(NCS)_2(phen)_2]$, 2.005 (5) Å in $[Cu(NCS)(phen)_2]^+$ (Parker, Manson & Breneman, 1994) and 1.945 (4) Å in $[Cu(NCS)_2(phen)]$ (Breneman & Parker, 1993). The thiocyanate ions are linear [178.9 (6)°] and are at an angle of 161.0 (6)° from the Cu atom in $[Cu(NCS)_2(phen)_2]$.

Experimental

cis-$[Cu^{II}(NCS)_2(phen)_2]$ was prepared by the slow addition of a 25 ml solution of 1,10-phenanthroline monohydrate (3.97 g, 20.0 mmol) in ethanol to a 20 ml solution of $CuCl_2.2H_2O$ (1.71 g, 10.0 mmol) dissolved in water. To the resulting solution, which contained a pale green precipitate, solid NH_4SCN (1.52 g, 20.0 mmol) was slowly added with continuous stirring. The light-green solid was dissolved in dimethyl sulfoxide and bright green crystals were obtained by evaporation of the solvent.

Crystal data

$[Cu(NCS)_2(C_{12}H_8N_2)_2]$
$M_r = 540.12$
Orthorhombic
Pbcn
$a = 13.224 (2)$ Å
$b = 10.058 (1)$ Å
$c = 17.423 (2)$ Å
$V = 2317.3 (5)$ Å^3
$Z = 4$
$D_x = 1.548$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.2–14.9°$
$\mu = 1.15$ mm^{-1}
$T = 293$ K
Hexagonal prism
0.30 × 0.20 × 0.15 mm
Light green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.65$, $T_{max} = 1.00$
2321 measured reflections
2321 independent reflections

1293 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
1 standard reflection frequency: 167 min intensity decay: 0.04%

Refinement

Refinement on F
$R = 0.04$
$wR = 0.07$
$S = 2.48$
1293 reflections
167 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0	0.15974 (9)	3/4	3.64 (2)
S	−0.1402 (2)	0.4722 (2)	0.9232 (1)	6.15 (4)
N1	−0.0330 (4)	0.2977 (5)	0.8305 (3)	5.3 (1)
N2	0.0025 (4)	0.0112 (5)	0.6627 (3)	4.05 (9)
N3	−0.1625 (4)	0.1298 (5)	0.7240 (3)	3.9 (1)
C1	−0.0782 (4)	0.3699 (6)	0.8685 (4)	4.2 (1)

C2	0.0822 (5)	−0.0425 (7)	0.6304 (4)	5.3 (2)
C3	0.0781 (5)	−0.1397 (7)	0.5743 (4)	6.0 (2)
C4	−0.0144 (5)	−0.1824 (7)	0.5497 (4)	5.7 (2)
C5	−0.1025 (5)	−0.1268 (6)	0.5809 (3)	4.4 (1)
C6	−0.2015 (5)	−0.1652 (7)	0.5593 (4)	5.3 (1)
C7	−0.2839 (5)	−0.1081 (7)	0.5908 (4)	5.2 (1)
C8	−0.2748 (4)	−0.0071 (6)	0.6473 (3)	4.2 (1)
C9	−0.3574 (5)	0.0576 (7)	0.6815 (4)	5.2 (2)
C10	−0.3415 (5)	0.1532 (6)	0.7351 (4)	5.2 (2)
C11	−0.2423 (5)	0.1849 (6)	0.7543 (4)	4.7 (1)
C12	−0.1779 (4)	0.0331 (6)	0.6708 (3)	3.6 (1)
C13	−0.0900 (4)	−0.0290 (6)	0.6375 (3)	3.7 (1)

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

Cu—N1	2.020 (7)	C4—C5	1.402 (9)
Cu—N2	2.132 (5)	C5—C6	1.415 (9)
Cu—N3	2.217 (5)	C5—C13	1.403 (8)
S—C1	1.625 (8)	C6—C7	1.35 (1)
N1—C1	1.150 (8)	C7—C8	1.419 (9)
N2—C2	1.311 (8)	C8—C9	1.404 (9)
N2—C13	1.361 (8)	C8—C12	1.404 (8)
N3—C11	1.303 (8)	C9—C10	1.357 (9)
N3—C12	1.359 (8)	C10—C11	1.39 (1)
C2—C3	1.38 (1)	C12—C13	1.442 (9)
C3—C4	1.366 (9)		
N1—Cu—N1^{i}	93.2 (4)	N2—C2—C3	124.3 (7)
N1—Cu—N2	168.4 (2)	C2—C3—C4	118.6 (7)
N1—Cu—N2^{i}	89.0 (2)	C3—C4—C5	119.8 (7)
N1—Cu—N3	91.5 (2)	C4—C5—C6	123.8 (7)
N1—Cu—N3^{i}	99.3 (2)	C4—C5—C13	117.0 (6)
N2—Cu—N2^{i}	91.1 (3)	C6—C5—C13	119.2 (6)
N2—Cu—N3	76.9 (2)	C5—C6—C7	121.6 (7)
N2—Cu—N3^{i}	92.0 (2)	C6—C7—C8	121.2 (6)
N3—Cu—N3^{i}	164.4 (3)	C7—C8—C9	124.1 (6)
Cu—N1—C1	161.0 (6)	C7—C8—C12	119.0 (6)
Cu—N2—C2	127.4 (5)	C9—C8—C12	116.9 (6)
Cu—N2—C13	115.1 (4)	C8—C9—C10	120.0 (7)
C2—N2—C13	117.5 (5)	C9—C10—C11	118.3 (7)
Cu—N3—C11	130.1 (4)	N3—C11—C10	124.7 (6)
Cu—N3—C12	112.5 (4)	N3—C12—C8	122.8 (6)
C11—N3—C12	117.3 (5)	N3—C12—C13	117.6 (5)
C8—C12—C13	119.6 (5)	N2—C13—C12	117.8 (5)
N2—C13—C5	122.8 (6)	C5—C13—C12	119.4 (6)
S—C1—N1	178.9 (6)		

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *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: *SHELXTL/PC*, *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Cu_3(bdmap)_4Cl_2(CH_3OH)$, bdmap = 1,3-Bis(dimethylamino)-2-propanolato. A Clamp-Shaped Molecule

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Abstract

The title structure, bis[μ-1,3-bis(dimethylamino)-2-propanolato]-1κN:2$\kappa N'$,1:2$\kappa^2 O$;1κN:3$\kappa N'$,1:3$\kappa^2 O$-bis[1,3-bis(dimethylamino)-2-propanolato]-2κN,2κO;3κN,3κO-dichloro-2κCl,3κCl-methanol-1κO-tricopper(II), [$Cu_3Cl_2(C_7H_{17}N_2O)_4(CH_4O)$], contains discrete molecules with C_2 crystallographic symmetry and a non-linear Cu_3 arrangement. Each Cu atom is five-coordinate. The central Cu atom is coordinated by a methanol molecule and is bridged by one bdmap ligand [bdmap = 1,3-bis(dimethylamino)-2-propanolato] to each of the outer Cu atoms, which are additionally coordinated by a Cl atom and a chelating bdmap ligand.

Comment

We have been investigating the coordination chemistry of copper(II) with bidentate and tridentate aminoalcohol ligands. Aminoalcohol ligands have been found to be