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Isothiocyanatobis(1,10-phenanthroline)-copper(II) Dicyanonitrosomethanide

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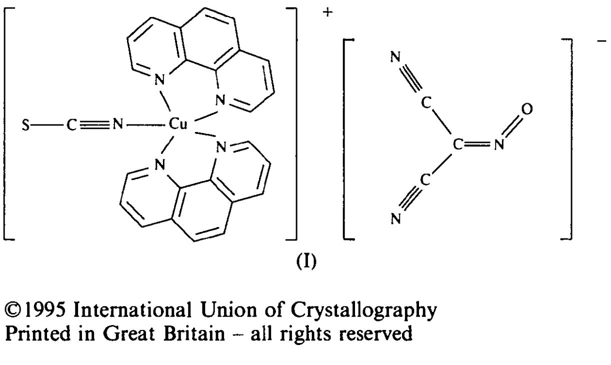
Abstract

The crystal structure of the title complex, $[Cu(NCS)(C_{12}H_8N_2)_2][ONC(CN)_2]$, (I), is presented. The structure is formed by discrete $[Cu(phen)_2(NCS)]^+$ cations and ndcm anions [phen = 1,10-phenanthroline, ndcm = dicyanonitrosomethanide, $ONC(CN)_2^-$]. The Cu atom is coordinated by five N atoms in the form of a distorted trigonal bipyramid with the chromophore CuN_5.

Comment

The title compound, (I), was prepared and its crystal structure solved as part of our study concerning changes in the shape of the $[Cu(phen)_2X]^+$ cation (X = a pseudohalide anion) caused by alteration of the out-of-sphere anion. Our previous attempts to prepare a compound with $X = NCS^-$ did not result in a complex in which NCS^- was coordinated to the Cu^{II} ion (Potočňák, Dunaj-Jurčo, Kabešová, Mikloš & Kettmann, 1994; Dunaj-Jurčo, Kabešová, Kettman, Císařová & Mikloš, 1993). Therefore, we decided to try to prepare a compound containing the $[Cu(phen)_2(NCS)]^+$ cation by using a reaction mixture containing both NCS^- and ndcm anions (ndcm = dicyanonitrosomethanide), expecting that the large ndcm anion would not enter the inner coordination sphere. The result was the title complex, (I), which contains discrete $[Cu(phen)_2(NCS)]^+$ cations and $ONC(CN)_2^-$ anions.



(I)

Fig. 1 shows one formula unit of (I) with the atomic labelling scheme. The Cu atom is coordinated by five N atoms from two phen molecules and an NCS^- ligand. The coordination polyhedron is in the form of a distorted trigonal bipyramid with the N atom of the NCS^- ligand in the equatorial plane. The ndcm anion does not enter the inner coordination sphere. The two out-of-plane Cu—N bonds, Cu1—N11 and Cu1—N13, are similar in length (average 1.987 Å) and are almost collinear [N11—Cu1—N13 172.24 (11)°]. The two in-plane Cu—N(phen) bonds (Cu1—N12 and Cu1—N14) are not significantly different in length either (average 2.092 Å) but they are longer than the out-of-plane Cu—N distances by an average of 0.105 Å. The third in-plane Cu—N bond [Cu1—N1 1.963 (3) Å] is significantly shorter than the other two. A recently published paper (Parker, Manson & Breneman, 1994) describes the structure of $[Cu(phen)_2NCS]ClO_4$, in which the corresponding out-of-plane and in-plane distances are somewhat longer [average 2.002 (4) Å] and somewhat shorter [average 2.069 (4) Å], respectively, but the Cu—N(NCS) distance is substantially longer [2.005 (4) Å]. The out-of-plane angles in the title complex lie within the range 80.5 to 95.9° (the range is 80.4 to 97.6° in the perchlorate). The

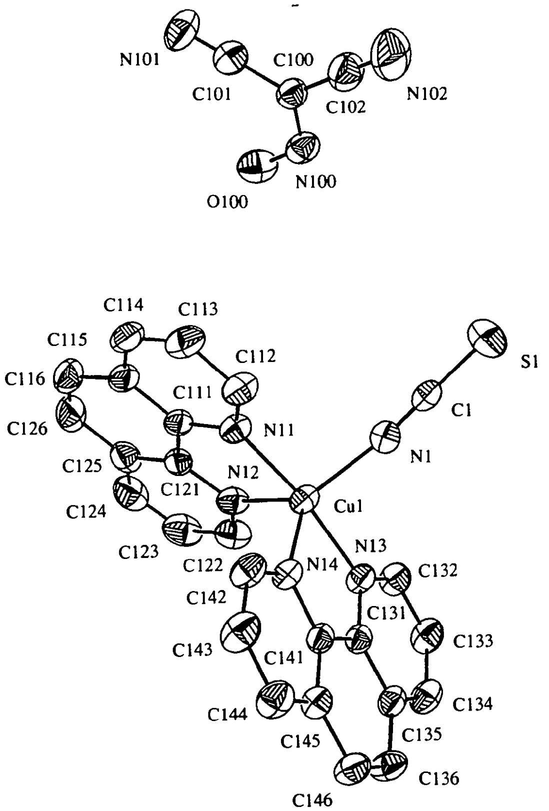


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title complex with the atom-labelling scheme. Displacement ellipsoids are shown at the 40% probability level.

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bond angles in the equatorial plane of the title complex differ considerably from the ideal trigonal angle of 120°, with one large angle of 127.96 (12)° (α_1 = N1—Cu1—N12) and two small angles of 115.81 (12)° (α_2 = N1—Cu1—N14) and 116.21 (10)° (α_3 = N12—Cu1—N14) [125.9 (2), 118.0 (2) and 116.1 (1)°, respectively, for the perchlorate]. Thus, the Cu1—N1 bond is shortened relative to a regular trigonal-bipyramidal $\mathrm{CuN_5}$ chromophore. The angle α_3, which is opposite the Cu1—N1 bond, is narrower than the ideal angle of 120° by 3.79°, and there is a difference of 12.15° between α_1 and α_2. According to Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as trigonal bipyramidal with near C_{2v} symmetry. The sum of the bond angles in the equatorial plane (359.98°) indicates coplanarity of the Cu atom with the three equatorial N atoms (the deviation of the Cu atom from the N1–N12–N14 plane is 0.018 Å).

The N atoms of the two phen molecules are coordinated both in equatorial and axial positions as a result of steric effects. The bond distances and angles in the phen molecules are normal (Anderson, 1973) and range from 1.312 to 1.427 Å and 116.5 to 125.0°, respectively. Both phen molecules are nearly planar (the largest deviation of an atom from the mean planes through the phen molecules is less than 0.050 Å). The mean planes of the two phen molecules are inclined at 110.0°.

The thiocyanate ligand is bound to the Cu atom through the N atom. The anion is linear [N1—C1—S1 178.2 (3)°] with N1—C1 and C1—S1 bond lengths of 1.140 (4) and 1.603 (4) Å, respectively. The coordination of the $\mathrm{NCS^-}$ anion to the Cu atom involves a significant deviation of the Cu1—N1—C1 angle, 171.1 (3)°, from linearity. This angle is 166.1 (5)° in the analogous perchlorate; other values are comparable.

The almost planar ndcm anion (the largest deviation of atoms from the mean plane is less than 0.014 Å) is uncoordinated, probably due to steric repulsion, and serves as a counterion to the $[\mathrm{Cu(phen)_2(NCS)}]^+$ cation. The mode of bonding in this anion can be described as largely delocalized π bonding (Golub, Köhler & Skopenko, 1986). According to this assumption, the lengths of the O100—N100 [1.246 (4) Å] and C100—N100 [1.334 (5) Å] bonds are somewhat longer than double O=N and C=N bonds (1.215 and 1.287 Å, respectively) and the C100—C101(C102) bond lengths [1.409 (5) and 1.408 (6) Å, respectively] are shorter than a single C—C bond (1.440 Å). On the other hand, the C101—N101 and C102—N102 bond lengths [1.125 (5) and 1.116 (6) Å, respectively] are somewhat shorter than a normal triple C≡N bond. Except for the C100—N100 bond, all these bonds are shorter than those found in $\mathrm{K[ONC(CN)_2]}$ (Skopenko, Zub, Poraj-Koshits & Sadikov, 1979). The O100—N100—C100, C101—C100—C102 and N100—C100—C101(C102) angles range from 116.2 to 123.0° and the C100—C101(C102)—N101(N102) angles are almost linear.

Experimental

The title complex was prepared by mixing 5 ml of a 1 *M* aqueous solution of $\mathrm{Cu(NO_3)_2}$ with 8 ml of $\mathrm{NH_4OH}$ and 20 ml of an ethanol solution of phen. A mixture of 5 ml of an aqueous solution of $\mathrm{NaONC(CN)_2}$ and 3 ml of an aqueous solution of KSCN in the molar ratio Cu:phen:$\mathrm{NaONC(CN)_2}$:KSCN 1:2:1.3:1 was then added. After several days prismatic dark green crystals of the title complex appeared. The density D_m was measured by flotation in $\mathrm{CCl_4}$–$\mathrm{CHBr_3}$.

Crystal data

$[\mathrm{Cu(NCS)(C_{12}H_8N_2)_2}]$-
$[\mathrm{ONC(CN)_2}]$
$M_r = 576.09$
Triclinic
$P\overline{1}$
$a = 7.937\ (4)$ Å
$b = 11.249\ (6)$ Å
$c = 15.144\ (6)$ Å
$\alpha = 99.59\ (4)°$
$\beta = 98.00\ (4)°$
$\gamma = 110.59\ (4)°$
$V = 1219.1\ (10)$ Å^3
$Z = 2$
$D_x = 1.569$ Mg m^{-3}
$D_m = 1.54\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 4.60$–$10.68°$
$\mu = 1.023$ mm^{-1}
$T = 295\ (2)$ K
Prism
0.30 × 0.15 × 0.12 mm
Dark green

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: none
5656 measured reflections
5656 independent reflections
3721 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 27.57°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = -19 \rightarrow 19$
2 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0506$
$wR(F^2) = 0.1112$
$S = 1.083$
5656 reflections
400 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.3278P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.438$ e Å^{-3}
$\Delta\rho_{\min} = -0.469$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992)

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

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

	x	y	z	U_{eq}
Cu1	0.36811 (5)	0.42657 (4)	0.22709 (3)	0.04323 (14)
N11	0.5757 (4)	0.5334 (3)	0.3318 (2)	0.0425 (6)
N12	0.3393 (4)	0.2917 (3)	0.3084 (2)	0.0437 (6)
N13	0.1782 (3)	0.3036 (3)	0.1185 (2)	0.0424 (6)
N14	0.5368 (3)	0.4228 (2)	0.1322 (2)	0.0394 (6)
S1	0.1668 (2)	0.77364 (12)	0.24807 (9)	0.0841 (4)
C1	0.2226 (5)	0.6491 (4)	0.2391 (2)	0.0458 (8)
N1	0.2624 (4)	0.5605 (3)	0.2303 (2)	0.0566 (8)
C111	0.6045 (4)	0.4686 (3)	0.3960 (2)	0.0412 (7)

C112	0.6873 (5)	0.6564 (4)	0.3431 (2)	0.0534 (9)
C113	0.8339 (6)	0.7191 (4)	0.4163 (3)	0.0610 (10)
C114	0.8653 (5)	0.6540 (4)	0.4805 (3)	0.0593 (10)
C115	0.7489 (5)	0.5248 (4)	0.4724 (2)	0.0494 (8)
C116	0.7686 (6)	0.4486 (5)	0.5362 (3)	0.0620 (11)
C121	0.4776 (5)	0.3382 (3)	0.3832 (2)	0.0425 (7)
C122	0.2180 (6)	0.1721 (4)	0.2970 (3)	0.0559 (9)
C123	0.2284 (7)	0.0952 (4)	0.3577 (3)	0.0679 (11)
C124	0.3676 (7)	0.1412 (5)	0.4316 (3)	0.0693 (12)
C125	0.4994 (6)	0.2668 (4)	0.4470 (2)	0.0542 (9)
C126	0.6512 (7)	0.3274 (5)	0.5238 (3)	0.0682 (12)
C131	0.2464 (4)	0.2738 (3)	0.0449 (2)	0.0379 (7)
C132	−0.0005 (5)	0.2474 (4)	0.1125 (3)	0.0523 (9)
C133	−0.1190 (5)	0.1575 (4)	0.0353 (3)	0.0558 (9)
C134	−0.0512 (5)	0.1262 (4)	−0.0384 (3)	0.0544 (9)
C135	0.1366 (4)	0.1857 (3)	−0.0359 (2)	0.0428 (7)
C136	0.2209 (5)	0.1623 (4)	−0.1100 (3)	0.0556 (9)
C141	0.4382 (4)	0.3391 (3)	0.0518 (2)	0.0378 (7)
C142	0.7143 (5)	0.4841 (4)	0.1394 (2)	0.0503 (9)
C143	0.8017 (5)	0.4669 (4)	0.0691 (3)	0.0592 (10)
C144	0.7049 (5)	0.3824 (4)	−0.0111 (2)	0.0548 (9)
C145	0.5167 (4)	0.3148 (3)	−0.0219 (2)	0.0430 (7)
C146	0.4017 (5)	0.2223 (4)	−0.1037 (2)	0.0542 (9)
O100	0.1742 (4)	0.6516 (3)	0.7155 (2)	0.0734 (8)
N100	0.1715 (4)	0.7427 (3)	0.6791 (2)	0.0595 (8)
C100	0.2965 (5)	0.8619 (4)	0.7198 (2)	0.0511 (8)
C101	0.4286 (5)	0.8878 (4)	0.8004 (3)	0.0566 (9)
N101	0.5300 (5)	0.9044 (4)	0.8654 (3)	0.0812 (11)
C102	0.2905 (7)	0.9631 (5)	0.6775 (3)	0.0758 (12)
N102	0.2803 (8)	1.0415 (5)	0.6431 (4)	0.125 (2)

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

Cu1—N1	1.963 (3)	O100—N100	1.246 (4)
Cu1—N11	1.980 (3)	N100—C100	1.334 (5)
Cu1—N13	1.994 (3)	C100—C101	1.409 (5)
Cu1—N12	2.080 (3)	C100—C102	1.408 (6)
Cu1—N14	2.101 (3)	C101—N101	1.125 (5)
S1—C1	1.603 (4)	C102—N102	1.116 (6)
C1—N1	1.140 (4)		
N1—Cu1—N11	93.63 (13)	N12—Cu1—N14	116.21 (10)
N1—Cu1—N13	93.91 (12)	N1—C1—S1	178.2 (3)
N11—Cu1—N13	172.24 (11)	C1—N1—Cu1	171.1 (3)
N1—Cu1—N12	127.96 (12)	O100—N100—C100	117.3 (3)
N11—Cu1—N12	80.90 (12)	N100—C100—C101	123.0 (4)
N13—Cu1—N12	95.87 (12)	N100—C100—C102	116.2 (3)
N1—Cu1—N14	115.81 (12)	C101—C100—C102	120.8 (4)
N11—Cu1—N14	94.57 (11)	N101—C101—C100	177.5 (4)
N13—Cu1—N14	80.46 (11)	N102—C102—C100	178.0 (6)

Data collection and cell refinement were carried out using Syntex $P2_1$ software. Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčík, 1993). The structure was solved by direct methods using *XFPS* (Pavelčík, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H-atoms were located from difference Fourier maps and refined with isotropic displacement factors fixed to 0.05 Å^2. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93. *ORTEP* (Johnson, 1965) was employed to draw the structure.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: KA1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-bromopyrazole)dichlorocopper(II)

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Abstract

The structure consists of *trans*-square-planar [$CuCl_2(C_3H_3BrN_2)_2$] units linked through Cu···Cl bonds giving each Cu^{II} atom [4 + 2] coordination.

Comment

This report extends work on metal coordination of halogenated nitrogen ligands (Valle, Sánchez González & Ettorre, 1991, 1993; Casellato, Graziani, Peruzzo & Plazzogna, 1994). The title structure, (I), consists of *trans*-square-planar [$CuCl_2(C_3H_3BrN_2)_2$] units linked through Cu···Cl bonds giving each Cu^{II} atom [4 + 2] coordination. The molecules form chains along the [100] direction by doubling-chloride bridging. The bonding

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