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Cyanobis(1,10-phenanthroline-*N,N'*)-copper(II) Isothiocyanate–Phenanthroline–Water (2/1/5.5)

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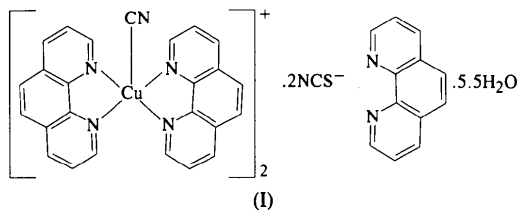
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Abstract

The crystal structure of the title complex, [Cu(CN)(C₁₂H₈N₂)₂]₂(NCS)₂·C₁₂H₈N₂·5.5H₂O, consists of discrete [Cu(CN)(phen)₂]⁺ cations (phen is 1,10-phenanthroline), NCS[−] anions and uncoordinated phen and water molecules. The two symmetrically independent Cu atoms are coordinated by four N atoms (from two phen molecules) and by one C atom (from the cyanide group) in the form of a distorted trigonal bipyramid (the C atom is in the equatorial plane).

Comment

The title compound, (I), was prepared and its crystal structure solved as part of a study concerning the changes in shape of the [CuX(phen)₂]⁺ cation (X[−] is a pseudo-halide anion) caused by alteration of the out-of-sphere anion.



The two [Cu(CN)(phen)₂]⁺ cations are shown in Fig. 1 with the atomic labelling, and the asymmetric part of the structure is shown in Fig. 2. The two symmetrically-independent Cu atoms are coordinated by four N atoms from the two phen molecules and by a C atom from the CN[−] group, creating a CuN₄C chromophore. The coordination polyhedra are

in the form of a distorted trigonal bipyramid with the cyano C atom in the equatorial plane. The NCS[−] anions, the water molecules and the remaining phen molecule do not enter the inner coordination sphere. The same [Cu(CN)(phen)₂]⁺ cation has been found in the structures of the [Cu(phen)₂(CN)]NO₃·H₂O (Anderson, 1975), [Cu^{II}(phen)₂(CN)][Cu^I(phen)₂(CN)₂].5H₂O (Dunaj-Jurčo, Potočnák, Cívik, Kabešová, Kettmann & Mikloš, 1993) and [Cu(phen)₂(CN)][C(CN)₃].2H₂O (Potočnák, Dunaj-Jurčo, Mikloš & Jäger, 1996) complexes. The two out-of-plane Cu—N bonds in the first coordination polyhedron (Cu1—N11 and Cu1—N13) are practically of the same length [average 2.008 (4) Å] and are almost collinear [N11—Cu1—N13 170.8 (3)]. The two in-plane Cu—N bonds (Cu1—N12 and Cu1—N14) are significantly different in length [2.085 (6) and 2.129 (6) Å, respectively] and their mean is longer by 0.099 Å than the mean of the out-of-plane Cu1—N distances. The third in-plane bond [Cu1—C1 1.948 (8) Å] is significantly shorter than the other two Cu—N in-plane bonds. The out-of-plane angles lie within the range 80.2 (2)–96.2 (3)°.

Similar features are observed in the geometry of the second coordination polyhedron. The out-of-plane Cu—N bonds (Cu2—N21 and Cu2—N23) average 2.006 (6) Å and the angle between them is 169.7 (3)°. The two in-plane Cu—N bonds (Cu2—N22 and Cu2—

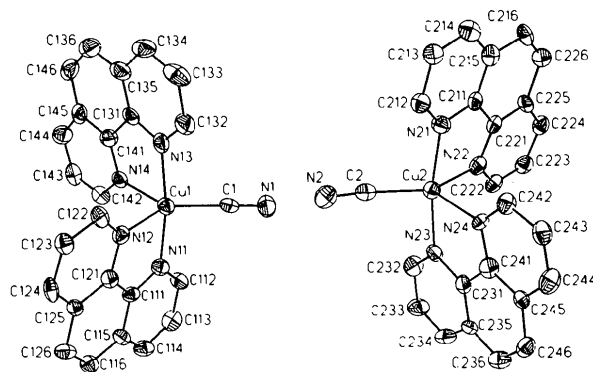


Fig. 1. ORTEP (Johnson, 1965) drawing of the cations showing the atom labelling. Displacement ellipsoids are plotted at the 40% probability level.

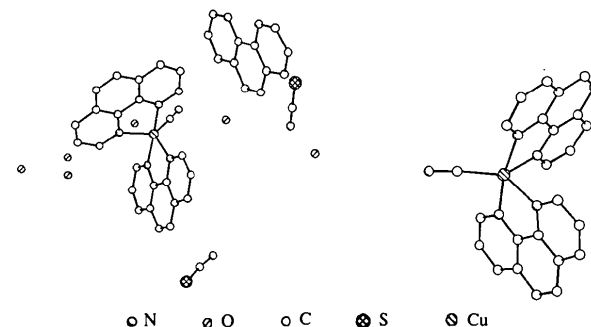


Fig. 2. The asymmetric part of the title structure.

N24) are not significantly different in length [average 2.119 (4) Å]; the difference between the averages of the in-plane and out-of-plane bonds is 0.113 Å. The Cu2—C2 bond distance is 1.947 (8) Å and the range of out-of-plane angles is 80.8 (2)–98.1 (3)°. The bond angles in the equatorial planes of both polyhedra differ considerably from the ideal trigonal angle of 120°, with one small and two large angles. In the first polyhedron, these angles are α_1 (C1—Cu1—N12) 135.8 (3), α_2 (C1—Cu1—N14) 126.7 (3) and α_3 (N12—Cu1—N14) 97.4 (2)°. The corresponding angles in the second polyhedron are α_1 (C2—Cu2—N22) 135.8 (3), α_2 (C2—Cu2—N24) 126.6 (3) and α_3 (N22—Cu2—N24) 97.5 (2)°. Thus, the Cu1—C1 and Cu2—C2 bonds are shortened relative to a regular trigonal-bipyramidal CuN₅ chromophore. The α_3 angles, which are opposite the Cu1—C1 and Cu2—C2 bonds, are narrower than the ideal angle of 120° by 22.6 and 22.5°, respectively. There is a difference between α_1 and α_2 of 9.1 and 9.2° in the first and second polyhedra, respectively. The coordination polyhedra around the two Cu atoms can therefore be described best as trigonal bipyramidal with near C_{2v} symmetry (Harrison & Hathaway, 1980). The sums of the bond angles in the equatorial planes (359.9 and 359.9°) indicate coplanarity of the Cu atoms with their three corresponding equatorial atoms [the Cu1 atom deviates by 0.026 (2) Å from the C1/N12/N14 plane and the Cu2 atom deviates by 0.039 (2) Å from the C2/N22/N24 plane].

The N atoms of the two phen molecules in both polyhedra are coordinated both in equatorial and axial positions, probably as a result of steric effects. The C—C bond distances and C—C angles in the phen molecules are quite normal and range from 1.353 (12) to 1.470 (10) Å and from 116.4 (6) to 124.1 (7)° in the first polyhedron, and from 1.337 (11) to 1.483 (10) Å and from 116.1 (7) to 124.5 (7)° in the second polyhedron. The phen molecules are nearly planar [the largest atomic deviation from the mean planes through the phen molecules is 0.037 (8) Å in the first polyhedron and 0.044 (9) Å in the second polyhedron]. The mean planes of the two phen molecules are inclined at angles of 87.9 (1) and 88.1 (1)° for the first and second polyhedra, respectively.

The cyanide groups are almost collinearly bound to the Cu atoms through the C atoms [Cu1—C1—N1 178.0 (7) and Cu2—C2—N2 173.0 (7)°], with C1—N1 and C2—N2 bond lengths of 1.152 (10) and 1.178 (10) Å, respectively.

The two NCS⁻ anions are uncoordinated and serve as counterions to the two [Cu(CN)(phen)₂]⁺ cations. One of these anions is linear [N3—C3—S3 179.1 (7)°], with N3—C3 and C3—S3 bond lengths of 1.186 (9) and 1.638 (8) Å, respectively, while the second anion is slightly bent [N4—C4—S4 171.4 (11)°], with N4—C4 and C4—S4 bond lengths of 1.214 (14) and 1.604 (12) Å, respectively.

There is another phen molecule which is uncoordinated. The C—C bond distances range from 1.344 (11) to 1.462 (11) Å and the C—C—C angles range from 117.5 (7) to 121.3 (7)°. This molecule is not as planar as the coordinated phen molecules [the largest atomic deviation from the mean plane through the phen molecule is 0.071 (9) Å].

Uncoordinated water molecules are involved in a rather complicated hydrogen-bonding system. The possible hydrogen bonds according to criterion of O···O and O···N distances less than 3.0 Å are given in Table 3. The s.o.f. of the O6 water molecule is 0.5.

Experimental

Crystals of (I) were prepared by mixing 10 ml of a 0.1 M aqueous solution of Cu(NO₃)₂ with 20 ml of a 0.1 M ethanol solution of phen. A mixture of 10 ml of a 0.1 M aqueous solution of KNCS and 10 ml of a 0.1 M aqueous solution of KCN was added. Crystals of (I) appeared after several weeks. The density D_m was measured by flotation in benzene/bromofrom/chloroform solution.

Crystal data

[Cu(CN)(C₁₂H₈N₂)₂]₂-
(NCS)₂·C₁₂H₈N₂·5.5H₂O
 $M_r = 1295.39$
Orthorhombic
 $P2_12_12_1$
 $a = 10.175 (8) \text{ \AA}$
 $b = 14.146 (14) \text{ \AA}$
 $c = 39.58 (4) \text{ \AA}$
 $V = 5696 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.510 \text{ Mg m}^{-3}$
 $D_m = 1.46 (1) \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
Cell parameters from 22 reflections
 $\theta = 5.25\text{--}12.54^\circ$
 $\mu = 0.888 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$
Prism
0.55 × 0.40 × 0.25 mm
Grey-blue

Data collection

Siemens P4 diffractometer
 ω scans
Absorption correction:
none
6970 measured reflections
6671 independent reflections
5004 observed reflections
[$I > 2\sigma(I)$]
 $R_{\text{int}} = 0.0535$

$\theta_{\text{max}} = 25^\circ$
 $h = -1 \rightarrow 12$
 $k = -9 \rightarrow 16$
 $l = -1 \rightarrow 46$
3 standard reflections
monitored every 100 reflections
intensity decay: 4.5%

Refinement

Refinement on F^2
 $R(F) = 0.0673$
 $wR(F^2) = 0.2088$
 $S = 0.990$
6626 reflections
793 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 17.9673P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.071$

$\Delta\rho_{\text{max}} = 0.683 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.497 \text{ e \AA}^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.03 (3)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$				
	x	y	z	U_{eq}
Cu1	0.19054 (9)	0.22839 (7)	0.14379 (2)	0.0365 (2)
N11	0.1990 (6)	0.1264 (4)	0.1789 (1)	0.036 (2)
N12	0.3911 (6)	0.1987 (4)	0.1416 (1)	0.034 (2)
N13	0.2065 (6)	0.3400 (5)	0.1127 (1)	0.042 (2)
N14	0.2006 (6)	0.3394 (4)	0.1800 (1)	0.037 (2)
N1	-0.0597 (7)	0.1436 (5)	0.1110 (2)	0.051 (2)
C1	0.0320 (8)	0.1766 (5)	0.1233 (2)	0.033 (2)
C111	0.3220 (8)	0.0956 (5)	0.1854 (2)	0.033 (2)
C112	0.0993 (8)	0.0907 (5)	0.1968 (2)	0.040 (2)
C113	0.1189 (9)	0.0207 (6)	0.2213 (2)	0.046 (2)
C114	0.2428 (9)	-0.0122 (6)	0.2285 (2)	0.045 (2)
C115	0.3499 (8)	0.0250 (5)	0.2101 (2)	0.035 (2)
C116	0.4812 (8)	-0.0019 (5)	0.2152 (2)	0.037 (2)
C121	0.4243 (7)	0.1329 (5)	0.1650 (2)	0.035 (2)
C122	0.4859 (7)	0.2337 (6)	0.1226 (2)	0.037 (2)
C123	0.6161 (8)	0.2072 (5)	0.1267 (2)	0.038 (2)
C124	0.6537 (7)	0.1434 (6)	0.1505 (2)	0.038 (2)
C125	0.5561 (7)	0.1034 (5)	0.1713 (2)	0.030 (2)
C126	0.5815 (9)	0.0355 (5)	0.1971 (2)	0.040 (2)
C131	0.2221 (7)	0.4246 (5)	0.1275 (2)	0.036 (2)
C132	0.2081 (9)	0.3368 (7)	0.0792 (2)	0.051 (2)
C133	0.2256 (9)	0.4208 (7)	0.0598 (2)	0.059 (3)
C134	0.2417 (9)	0.5059 (7)	0.0751 (2)	0.055 (2)
C135	0.2392 (9)	0.5096 (6)	0.1109 (2)	0.052 (2)
C136	0.2501 (9)	0.5950 (6)	0.1296 (3)	0.060 (3)
C141	0.2186 (8)	0.4242 (6)	0.1647 (2)	0.044 (2)
C142	0.1967 (8)	0.3410 (6)	0.2136 (2)	0.046 (2)
C143	0.2091 (9)	0.4205 (7)	0.2325 (2)	0.053 (2)
C144	0.2266 (9)	0.5058 (6)	0.2178 (2)	0.053 (2)
C145	0.2334 (8)	0.5106 (6)	0.1823 (2)	0.047 (2)
C146	0.2507 (9)	0.5956 (7)	0.1640 (2)	0.055 (2)
Cu2	0.13084 (10)	0.65234 (6)	0.86715 (2)	0.0356 (2)
N21	0.1265 (7)	0.5479 (4)	0.9013 (1)	0.038 (2)
N22	-0.0714 (6)	0.6184 (4)	0.8646 (1)	0.037 (2)
N23	0.1065 (6)	0.7660 (4)	0.8373 (1)	0.037 (2)
N24	0.1171 (6)	0.7585 (4)	0.9049 (1)	0.031 (1)
N2	0.3799 (8)	0.5962 (5)	0.8258 (2)	0.052 (2)
C2	0.2889 (9)	0.6139 (5)	0.8431 (2)	0.040 (2)
C211	0.0036 (7)	0.5166 (5)	0.9087 (2)	0.032 (2)
C212	0.2257 (8)	0.5149 (5)	0.9187 (2)	0.037 (2)
C213	0.2111 (8)	0.4480 (6)	0.9447 (2)	0.043 (2)
C214	0.0886 (8)	0.4170 (6)	0.9528 (2)	0.042 (2)
C215	-0.0194 (8)	0.4511 (6)	0.9344 (2)	0.038 (2)
C216	-0.1537 (7)	0.4205 (6)	0.9401 (2)	0.039 (2)
C221	-0.1031 (7)	0.5543 (5)	0.8891 (2)	0.032 (2)
C222	-0.1695 (7)	0.6511 (5)	0.8461 (2)	0.037 (2)
C223	-0.2987 (9)	0.6257 (5)	0.8505 (2)	0.044 (2)
C224	-0.3318 (8)	0.5611 (5)	0.8754 (2)	0.042 (2)
C225	-0.2291 (7)	0.5250 (5)	0.8952 (2)	0.033 (2)
C226	-0.2545 (8)	0.4546 (5)	0.9222 (2)	0.039 (2)
C231	0.0937 (7)	0.8503 (5)	0.8547 (2)	0.033 (2)
C232	0.1021 (9)	0.7674 (6)	0.8037 (2)	0.046 (2)
C233	0.0839 (9)	0.8505 (6)	0.7854 (2)	0.049 (2)
C234	0.0673 (9)	0.9329 (5)	0.8027 (2)	0.042 (2)
C235	0.0742 (8)	0.9360 (5)	0.8381 (2)	0.033 (2)
C236	0.0649 (8)	1.0197 (5)	0.8576 (2)	0.040 (2)
C241	0.0971 (8)	0.8452 (6)	0.8910 (2)	0.039 (2)
C242	0.1188 (8)	0.7535 (5)	0.9384 (2)	0.038 (2)
C243	0.1057 (8)	0.8327 (6)	0.9590 (2)	0.043 (2)
C244	0.0881 (9)	0.9178 (6)	0.9448 (2)	0.047 (2)
C245	0.0830 (7)	0.9271 (5)	0.9092 (2)	0.032 (2)
C246	0.0690 (8)	1.0155 (6)	0.8921 (2)	0.042 (2)
N3	0.1949 (7)	0.3453 (5)	0.5009 (2)	0.048 (2)
N4	0.2244 (8)	0.7373 (5)	0.2543 (3)	0.087 (3)
C3	0.2168 (8)	0.2888 (6)	0.5223 (2)	0.042 (2)
C4	0.3318 (12)	0.7658 (7)	0.2630 (3)	0.078 (3)
S3	0.2452 (2)	0.2114 (2)	0.55218 (5)	0.0469 (5)
S4	0.4638 (3)	0.8059 (2)	0.27986 (6)	0.0604 (7)
N31	0.1183 (6)	-0.0992 (5)	0.3743 (1)	0.039 (2)
N32	0.1040 (7)	-0.0355 (5)	0.4401 (1)	0.043 (2)
C311	0.0998 (8)	-0.0048 (5)	0.3800 (2)	0.035 (2)
C312	0.1257 (8)	-0.1285 (5)	0.3424 (2)	0.039 (2)
C313	0.1162 (9)	-0.0662 (6)	0.3149 (2)	0.043 (2)
C314	0.0982 (8)	0.0269 (6)	0.3198 (2)	0.041 (2)
C315	0.0883 (7)	0.0596 (5)	0.3537 (2)	0.037 (2)
C316	0.0700 (8)	0.1592 (6)	0.3601 (2)	0.045 (2)
C321	0.0917 (8)	0.0284 (5)	0.4148 (2)	0.037 (2)
C322	0.0921 (9)	-0.0034 (7)	0.4712 (2)	0.054 (3)
C323	0.0678 (9)	0.0888 (7)	0.4796 (2)	0.055 (3)
C324	0.0532 (9)	0.1541 (7)	0.4543 (2)	0.054 (2)
C325	0.0691 (8)	0.1241 (6)	0.4209 (2)	0.044 (2)
C326	0.0607 (7)	0.1910 (6)	0.3929 (2)	0.042 (2)
O1	0.3566 (7)	0.2280 (4)	-0.0571 (1)	0.064 (2)
O2	0.0012 (6)	0.4522 (5)	0.4663 (2)	0.062 (2)
O3	0.0275 (8)	0.2465 (7)	0.2756 (2)	0.099 (3)
O4	0.0405 (9)	0.1498 (7)	0.0178 (2)	0.114 (3)
O5	0.5704 (12)	0.3134 (7)	0.0501 (2)	0.130 (4)
O6†	0.7422 (19)	0.2493 (10)	-0.0030 (3)	0.105 (6)

† Site occupancy factor of 0.5.

Table 2. Selected geometric parameters (Å, °)

Cu1—C1	1.948 (8)	Cu2—C2	1.947 (8)
Cu1—N11	2.005 (6)	Cu2—N21	2.002 (6)
Cu1—N13	2.010 (6)	Cu2—N23	2.010 (6)
Cu1—N12	2.085 (6)	Cu2—N24	2.122 (6)
Cu1—N14	2.129 (6)	Cu2—N22	2.116 (7)
N1—C1	1.152 (10)	N2—C2	1.178 (10)
C3—S3	1.638 (8)	C4—S4	1.604 (12)
N3—C3	1.186 (9)	N4—C4	1.214 (14)
C1—Cu1—N11	93.0 (3)	C2—Cu2—N21	98.1 (3)
C1—Cu1—N13	96.2 (3)	C2—Cu2—N23	92.2 (3)
N11—Cu1—N13	170.8 (3)	N21—Cu2—N23	169.7 (3)
C1—Cu1—N12	135.8 (3)	C2—Cu2—N24	126.6 (3)
N11—Cu1—N12	80.9 (2)	N21—Cu2—N24	92.6 (2)
N13—Cu1—N12	93.1 (2)	N23—Cu2—N24	80.8 (2)
C1—Cu1—N14	126.7 (3)	C2—Cu2—N22	135.8 (3)
N11—Cu1—N14	93.6 (2)	N21—Cu2—N22	81.0 (3)
N13—Cu1—N14	80.2 (2)	N23—Cu2—N22	91.9 (3)
N12—Cu1—N14	97.4 (2)	N24—Cu2—N22	97.5 (2)
N1—C1—Cu1	178.0 (7)	N2—C2—Cu2	173.0 (7)
N3—C3—S3	179.1 (7)	N4—C4—S4	171.4 (11)

Table 3. Contact distances (Å)

O1...N1 ⁱ	2.928 (9)	O2...O4 ^{iv}	2.895 (12)
O1...O4 ⁱ	2.984 (11)	O3...N4 ^v	2.827 (12)
O1...O5 ⁱⁱ	2.983 (14)	O4...O5 ⁱⁱ	2.755 (12)
O1...N32 ⁱⁱⁱ	2.755 (9)	O4...O6 ⁱⁱ	2.57 (2)
O1...O6 ⁱⁱ	2.667 (15)	O5...O6	2.879 (18)
O2...N3	2.836 (10)		

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (iii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

The title structure was solved by the heavy-atom method (XFP5; Pavelčík, Rizzoli & Andreotti, 1990) with subsequent Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. Due to the large displacement factor of the N4 atom, we tried to solve the structure with the atom split into two sites. The anisotropic refinement of the two atoms led, however, to physically unacceptable vibration directions (one perpendicular to the other). Even so, the relatively high $\Delta\rho_{\min}$ value remained unchanged. The $\Delta\rho$ minimum is far from any heavy atom and is close to a phen C atom (2 Å). We believe, therefore, that the minimum is a false minimum. A simpler model with an ordered N4 atom was thus refined. All phen H atoms were included in the refinement in calculated positions with fixed isotropic displacement parameters. Water H atoms were neither found nor calculated. Geometrical analysis was performed using PARST (Nardelli, 1983) and SHELXL93 (Sheldrick, 1993).

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to refine

structure: *SHELXL93*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Addition of Methanol to Copper(II)-Coordinated Dicyanonitrosomethanide: (3-Amino-3-methoxy-2-nitrosoacrylonitrilato-*N*²,*N*³)(bipyridine-*N*,*N*¹)(dicyanamido-*N*)copper(II)

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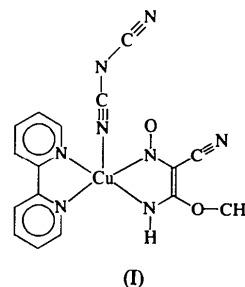
Abstract

A new ligand formation was observed in the title complex, [Cu(C₄H₄N₃O₂){N(CN)₂}(C₁₀H₈N₂)], as a result of the nucleophilic addition reaction between methanol and dicyanonitrosomethanide in the inner

coordination sphere of a Cu^{II} atom. This new ligand, 3-amino-3-methoxy-2-nitrosoacrylonitrilate (add), [NHC(OMe)C(CN)NO][−], is coordinated as a chelate, forming a five-membered metallacycle with Cu^{II}. The distorted tetragonal-pyramidal coordination is completed by one chelate-coordinated molecule of 2,2'-bipyridine (bipy) and one end-coordinated dicyanamide anion, [N(CN)₂][−]. The four N atoms of the two metallacycles form the base and a fifth N atom, from the dicyanamide anion, forms the apex of the pyramid, creating a {CuN₅} chromophore. The structure of [Cu(add)(bipy){N(CN)₂}] consists of discrete molecules.

Comment

The title compound, (I), was prepared and its crystal structure solved as a part of our study concerning changes in the shape of the [Cu(*N,N*-chel)₂X]⁺ cation resulting from alteration of the out-of-sphere anion Y[−] [*N,N*-chel = 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy), X[−] = the linear and non-linear pseudo-halide anions cyanide(1[−]), thiocyanate(1[−]) and dicyanamide(1[−]), and Y[−] = the non-linear pseudo-halide anions tricyanomethanide(1[−]) and dicyanonitrosomethanide(1[−])].



We have recently published several structures of Cu^{II} coordination compounds with phen, X[−] and Y[−]; [Cu(phen)₂{N(CN)₂}]₂ [(II); Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995a], [Cu(phen)₂{N(CN)₂}] [C(CN)₃] [(III); Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996c], [Cu(phen)₂(NCS)][C(CN)₃] [(IV); Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996b], [Cu(phen)₂(CN)][C(CN)₃].2H₂O [(V); Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996a] and [Cu(phen)₂(NCS)][ONC(CN)₂] [(VI); Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995b]. Dicyanamide anions complete the sixfold coordination of Cu^{II} in compound (II) and the fivefold coordination of Cu^{II} in (III). Tricyanomethanide and dicyanonitrosomethanide do not enter the inner coordination sphere of Cu^{II} in any of the above compounds. Also, no creation of new ligands in the coordination sphere of Cu^{II} has been observed in the above compounds.

On the other hand, when phen was replaced by bipy we obtained the title compound, [Cu(bipy){CH₃OH.-