
Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyanobis(1,10-phenanthroline)copper(II) Tricyanomethanide Dihydrate

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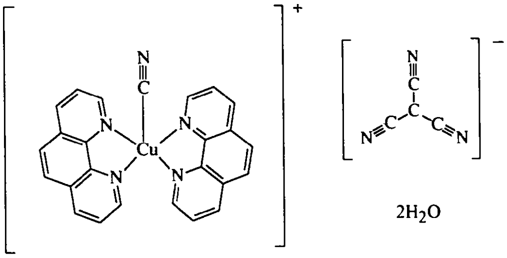
Abstract

The crystal structure of the title complex, $[Cu(CN)(C_{12}H_8N_2)_2][C(CN)_3].2H_2O$, is formed by discrete $[Cu(phen)_2(CN)]^+$ cations, tcm anions and uncoordinated water molecules [phen = 1,10-phenanthroline, tcm = tricyanomethanide, $C(CN)_3^-$]. The Cu atom is coordinated by four N atoms (from two phen molecules) and by one C atom (from the cyanide group in the equatorial plane) in the form of a distorted trigonal bipyramid.

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^- = pseudohalide anion) caused by variation of the out-of-sphere anion.



(I)

Recently, we determined the structure of $[Cu(phen)_2(NCS)][C(CN)_3]$ with X^- = NCS^- (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996). The tcm anion did not enter the inner coordination sphere of the Cu atom, probably because of steric repulsion. Rather than the bulky NCS^- anion, we investigated the smaller CN^- group to find out whether the large tcm anion would coordinate to the Cu atom to form a six-coordinate species. The result is the title complex, (I), with a five-coordinate Cu atom.

Fig. 1 shows one formula unit with the atomic labelling scheme. The Cu atom is coordinated by four N atoms from two phen molecules and by one C atom from the CN^- group. The coordination polyhedron is in the form of a distorted trigonal bipyramid with the C atom in the equatorial plane. Neither the tcm anion nor the two water molecules enter the inner coordination sphere. The same $[Cu(phen)_2(CN)]^+$ cation has been found in the structures of $[Cu(phen)_2(CN)]NO_3.H_2O$ (Anderson, 1975) and $[Cu^{II}(phen)_2(CN)][Cu^{I}(phen)_2(CN)_2].5H_2O$ (Dunaj-Jurčo *et al.*, 1993).

The two out-of-plane Cu—N bonds in (I) (Cu—N21 and Cu—N31) are practically of the same length (average 2.002 Å) and are almost collinear [N21—Cu—N31 = 169.92 (12)°]. The two in-plane Cu—N bonds (Cu—N11 and Cu—N41) are not significantly different in length either (average 2.106 Å) but they are longer than the out-of-plane Cu—N distances, on average by 0.104 Å. The third in-plane bond [Cu—

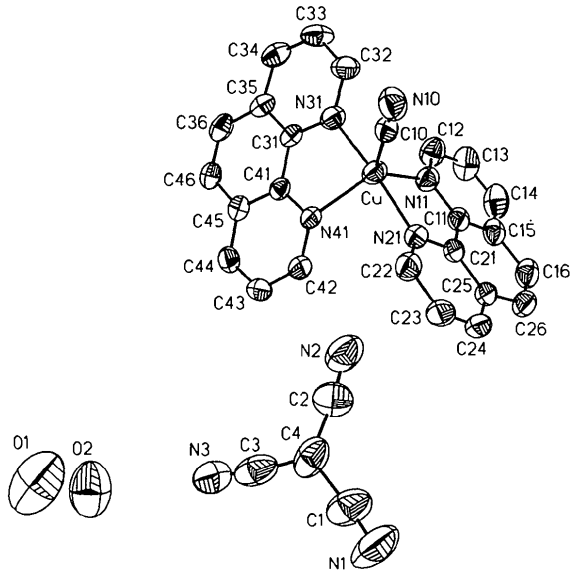


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the formula unit and labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

C10 = 1.970 (5) Å] is significantly shorter than the other two. The out-of-plane angles lie within the range 79.9–95.1°. The bond angles in the equatorial plane differ considerably from the ideal trigonal angle of 120°, with two large angles of 131.86 (14) (α_1 = C10—Cu—N41) and 124.80 (14)° (α_2 = C10—Cu—N11) and one small angle of 103.34 (11)° (α_3 = N11—Cu—N41). Thus, the Cu—C10 bond is shortened relative to that of a regular trigonal-bipyramidal CuN_4C chromophore. The angle α_3, which is opposite the Cu—C10 bond, is narrower than the ideal angle of 120° by 16.66°, and there is a difference of 7.06° between α_1 and α_2. Thus, the coordination polyhedron around the Cu atom can be best described as trigonal bipyramidal with near C_{2v} symmetry (Harrison & Hathaway, 1980). The sum of the bond angles in the equatorial plane (360.00°) indicates coplanarity of the Cu atom with the three equatorial atoms (the deviation of the Cu atom from the C10—N11—N41 plane is 0.003 Å).

The N atoms of the two phen molecules are coordinated both in equatorial and in axial positions, probably as a result of steric effects. The bond distances and angles in the phen molecules are normal and range from 1.328 to 1.431 Å and 116.1 to 124.6°, respectively. Both phen molecules are almost planar (the largest deviation of an atom from the mean planes through the phen molecules is less than 0.029 Å). The mean planes of the two phen molecules are inclined at 101.6 (5)°.

The cyanide group is linearly bound to the Cu atom through the C atom [Cu—C10—N10 = 177.6 (4)°] with a C10—N10 bond length of 1.122 (5) Å.

The almost planar tcm anion (the largest deviation of atoms from the mean plane is less than 0.043 Å) is uncoordinated, probably due to steric repulsion, and serves as a counterion to the $[Cu(phen)_2(CN)]^+$ cation. According to Golub, Köhler & Skopenko (1986), the mode of bonding in this anion can be described as largely delocalized π-bonding and C—C lengths of ~1.394 and C—N lengths of ~1.177 Å should be expected. On the contrary to this assumption, all of the lengths of the C4—C1, C4—C2 and C4—C3 bonds [1.452 (7), 1.405 (8) and 1.463 (9) Å, respectively] are longer, and C1—N1 and C2—N2 [1.098 (6) and 1.072 (6) Å, respectively] are shorter than the expected values. The longer C3—N3 bond length [1.188 (8) Å] is due to the N3···O2 hydrogen bond [2.860 (7) Å]. These results indicate localized C—C single bonds and localized C≡N triple bonds. The angles around the central C4 atom range from 118.8 to 120.9° and the C4—C1—N1, C4—C2—N2 and C4—C3—N3 angles range from 172.9 to 176.1°, indicating the sp^2 and sp hybridization of the appropriate C atoms.

The two water molecules are uncoordinated. The first H_2O (O1) molecule forms one hydrogen bond to the H_2O (O2) molecule and the second H_2O (O2) molecule forms three hydrogen bonds: O2···O1 = 2.735 (9), O2···N3 = 2.860 (7) and O2···N10 = 2.903 (9) Å. The latter two hydrogen bonds cause the prolongation of the multiple bonds C3—N3 [1.188 (8) Å] and C10—N10 [1.222 (5) Å].

Experimental

Crystals were prepared by mixing 10 ml of a 0.1 *M* water solution of $Cu(NO_3)_2$ with 20 ml of a 0.1 *M* ethanol solution of phen. A mixture of 10 ml of a 0.1 *M* ethanol solution of $KC(CN)_3$ and 10 ml of a 0.1 *M* water solution of KCN was added. Dark green prismatic crystals of (I) appeared the next day. The density D_m was measured by flotation in benzene–bromoform.

Crystal data

$[Cu(CN)(C_{12}H_8N_2)_2]$-
$[C(CN)_3].2H_2O$
$M_r = 576.07$
Triclinic
$P\bar{1}$
$a = 10.262\ (3)$ Å
$b = 10.595\ (3)$ Å
$c = 11.950\ (4)$ Å
$\alpha = 88.36\ (2)°$
$\beta = 84.28\ (2)°$
$\gamma = 83.07\ (2)°$
$V = 1283.2\ (7)$ Å^3
$Z = 2$
$D_x = 1.491$ Mg m^{-3}
$D_m = 1.47$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 4.85–11.87°$
$\mu = 0.896$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.45 × 0.45 × 0.25 mm
Dark green

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.756$, $T_{max} = 0.966$
4530 measured reflections
4530 independent reflections
2771 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 25.00°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
2 standard reflections monitored every 98 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0438$
$wR(F^2) = 0.1084$
$S = 1.094$
4525 reflections
425 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.706$ e Å^{-3}
$\Delta\rho_{min} = -0.245$ e Å^{-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)

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

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

	x	y	z	U_{eq}
Cu	0.18422 (5)	0.46747 (4)	0.23407 (4)	0.0521 (2)
N11	0.3358 (3)	0.3275 (3)	0.1699 (2)	0.0529 (8)
N21	0.3345 (3)	0.5725 (3)	0.2083 (2)	0.0496 (7)
N31	0.0561 (3)	0.3413 (3)	0.2739 (3)	0.0517 (8)
N41	0.1953 (3)	0.4537 (3)	0.4083 (2)	0.0446 (7)
C10	0.0670 (4)	0.5777 (4)	0.1417 (3)	0.0534 (10)
N10	−0.0008 (4)	0.6432 (4)	0.0921 (3)	0.0735 (10)
C11	0.4513 (4)	0.3764 (4)	0.1465 (3)	0.0489 (9)
C12	0.3353 (5)	0.2050 (4)	0.1498 (4)	0.0688 (12)
C13	0.4467 (6)	0.1284 (5)	0.1094 (4)	0.0813 (14)
C14	0.5619 (6)	0.1770 (5)	0.0851 (4)	0.0805 (15)
C15	0.5675 (4)	0.3064 (4)	0.1036 (3)	0.0587 (11)
C16	0.6825 (4)	0.3681 (6)	0.0772 (4)	0.0691 (13)
C21	0.4503 (4)	0.5089 (4)	0.1670 (3)	0.0483 (9)
C22	0.3305 (5)	0.6959 (4)	0.2298 (3)	0.0632 (11)
C23	0.4432 (5)	0.7581 (5)	0.2105 (4)	0.0690 (12)
C24	0.5566 (5)	0.6957 (5)	0.1683 (4)	0.0676 (13)
C25	0.5655 (4)	0.5659 (4)	0.1433 (3)	0.0561 (10)
C26	0.6822 (4)	0.4921 (5)	0.0965 (3)	0.0667 (12)
C31	0.0445 (3)	0.3065 (3)	0.3831 (3)	0.0464 (9)
C32	−0.0106 (4)	0.2854 (4)	0.2032 (4)	0.0650 (11)
C33	−0.0892 (5)	0.1916 (4)	0.2391 (5)	0.0756 (14)
C34	−0.1024 (4)	0.1578 (4)	0.3500 (4)	0.0675 (12)
C35	−0.0343 (3)	0.2144 (3)	0.4269 (3)	0.0524 (10)
C36	−0.0391 (4)	0.1834 (4)	0.5435 (4)	0.0601 (11)
C41	0.1189 (3)	0.3674 (3)	0.4562 (3)	0.0431 (8)
C42	0.2644 (4)	0.5105 (4)	0.4755 (3)	0.0535 (10)
C43	0.2612 (4)	0.4868 (4)	0.5896 (3)	0.0589 (11)
C44	0.1846 (4)	0.4000 (4)	0.6375 (3)	0.0574 (10)
C45	0.1103 (4)	0.3357 (3)	0.5709 (3)	0.0498 (9)
C46	0.0297 (4)	0.2410 (4)	0.6117 (4)	0.0578 (11)
C1	0.4779 (6)	1.2064 (5)	0.4605 (6)	0.107 (2)
N1	0.5459 (5)	1.2777 (6)	0.4381 (6)	0.150 (2)
C2	0.3218 (6)	1.0621 (5)	0.4129 (5)	0.085 (2)
N2	0.2682 (5)	1.0163 (5)	0.3565 (4)	0.1013 (15)
C3	0.3449 (5)	1.0973 (5)	0.6153 (7)	0.099 (2)
N3	0.3164 (5)	1.0688 (5)	0.7106 (5)	0.109 (2)
C4	0.3775 (5)	1.1241 (5)	0.4956 (6)	0.093 (2)
O1	0.1553 (7)	0.9350 (6)	1.0920 (7)	0.245 (4)
O2	0.1590 (5)	1.1114 (4)	0.9204 (4)	0.160 (2)

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

Cu—C10	1.970 (5)	C1—N1	1.098 (6)
Cu—N31	2.001 (3)	C1—C4	1.452 (7)
Cu—N21	2.003 (3)	C2—N2	1.072 (6)
Cu—N41	2.096 (3)	C2—C4	1.405 (8)
Cu—N11	2.116 (3)	C3—N3	1.188 (8)
C10—N10	1.122 (5)	C3—C4	1.463 (9)
C10—Cu—N31	95.10 (14)	N41—Cu—N11	103.34 (11)
C10—Cu—N21	94.93 (14)	N10—C10—Cu	177.6 (4)
N31—Cu—N21	169.92 (12)	N1—C1—C4	173.4 (7)
C10—Cu—N41	131.86 (14)	N2—C2—C4	172.9 (7)
N31—Cu—N41	80.49 (12)	N3—C3—C4	176.1 (6)
N21—Cu—N41	93.50 (11)	C2—C4—C1	118.8 (6)
C10—Cu—N11	124.80 (14)	C2—C4—C3	120.9 (5)
N31—Cu—N11	93.52 (12)	C1—C4—C3	120.1 (6)
N21—Cu—N11	79.92 (12)		

Anisotropic displacement parameters were refined for all non-H atoms. All phen H atoms were located from the difference Fourier map and refined with free isotropic temperature factors. Water H atoms were not found.

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 the heavy-atom method with *XFPS* (Pavelčík, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). 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 complete geometry have been deposited with the IUCr (Reference: KA1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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