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two phen molecules occupy both equatorial and axial positions. Recently, we have published the structure of a complex with the same general formula, with  $X = \text{N}(\text{CN})_2$ . The two dicyanamide ligands are also in a *cis* configuration but one occupies the axial while the second one the equatorial plane. One phen molecule occupies both the equatorial and the axial position, as in the previous cases, but the second phen molecule is coordinated only in the equatorial plane (Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995). We have also published structures of two five-coordinate  $[\text{Cu}(\text{phen})_2\text{X}][\text{C}(\text{CN})_3] \cdot n\text{H}_2\text{O}$  complexes, with  $X = \text{NCS}$ ,  $n = 0$  and  $X = \text{CN}$ ,  $n = 2$  (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996*a,b*). The phenanthroline molecules occupy both the equatorial and the axial positions, as in the six-coordinate compounds with  $X = \text{NCS}$  and  $\text{NCSe}$ . We decided to prepare a five-coordinate compound with  $X = \text{N}(\text{CN})_2$  to find out whether the coordination polyhedron around the  $\text{Cu}^{\text{II}}$  atom will be of the same type as in previous five-coordinate complexes or whether dicyanamide will induce differences in the coordination polyhedron similar to those of the six-coordinate complex  $[\text{Cu}(\text{phen})_2[\text{N}(\text{CN})_2]]$ .

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### (Dicyanamido)bis(1,10-phenanthroline)-copper(II) Tricyanomethanide

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#### Abstract

The crystal structure of  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2\{\text{N}(\text{CN})_2\}]^+[\text{C}(\text{CN})_3]^-$  is formed by discrete  $[\text{Cu}(\text{phen})_2\{\text{N}(\text{CN})_2\}]^+$  cations and  $[\text{C}(\text{CN})_3]^-$  anions (phen = 1,10-phenanthroline). The coordination polyhedron of  $\text{Cu}^{\text{II}}$  is a distorted trigonal bipyramid with a  $\text{CuN}_5$  chromophore.

#### Comment

Crystal structures of five-coordinate copper compounds with the general formula  $[\text{Cu}(\text{phen})_2\text{X}_2]$ , where  $X = \text{NCS}$  and  $\text{NCSe}$ , are known (Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1982). The pseudo-halide ligands are in a *cis* configuration in an equatorial plane and the

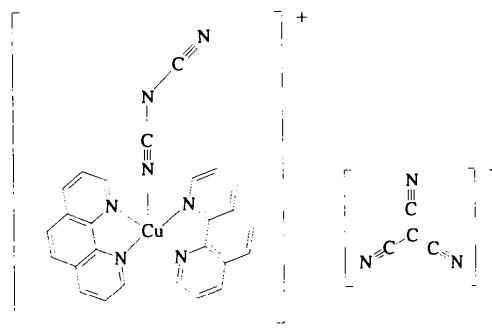


Fig. 1 shows the labelling scheme of one formula unit. The Cu atom is fivefold coordinated by two phen molecules and by one  $\text{N}(\text{CN})_2^-$  ligand (in the equatorial plane). The coordination polyhedron is a distorted trigonal bipyramid. The  $\text{tcm}^-$  anion  $\{[\text{C}(\text{CN})_3]^-$  does not enter the inner coordination sphere. In the trigonal bipyramid the two out-of-plane  $\text{Cu}-\text{N}11$  and  $\text{Cu}-\text{N}31$  distances are practically of the same length [1.977 (4) and 1.981 (3) Å, respectively] and are almost collinear [ $\text{N}11-\text{Cu}-\text{N}31 = 175.12 (14)^\circ$ ]. The two in-plane distances ( $\text{Cu}-\text{N}21$  and  $\text{Cu}-\text{N}41$ ) also have similar values [2.064 (3) and 2.112 (4) Å, respectively], but they are longer on average than the out-of-plane  $\text{Cu}-\text{N}$  distances by 0.109 Å. The third in-plane  $\text{Cu}-\text{N}2$  distance of 1.982 (4) Å is significantly shorter than the other two. The out-of-plane angles lie within the range  $80.7-95.2^\circ$ . The same features of the coordination polyhedron as well as similar values of the appropriate bond distances and angles were observed in the structures of both above five-coordinate Cu complexes with the same  $\text{tcm}^-$  counteranion.

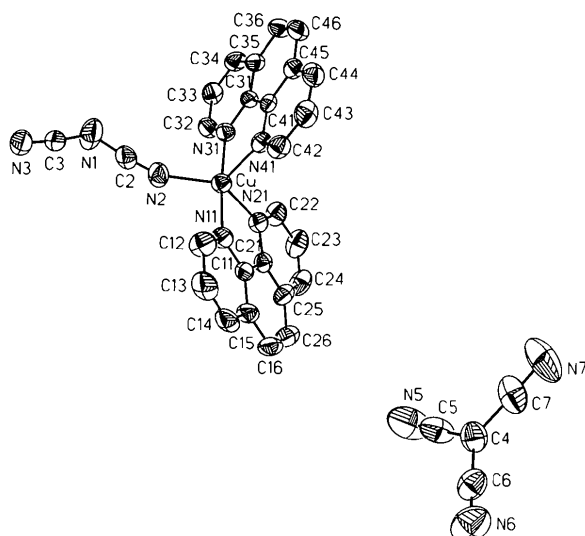


Fig. 1. ORTEP (Johnson, 1965) drawing of the formula unit and labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

The bond angles in the equatorial plane differ considerably from the ideal trigonal angle of  $120^\circ$ , with one large angle of  $133.6(2)^\circ$  ( $\alpha_1 = \text{N2—Cu—N21}$ ) and two small angles of  $115.7(2)^\circ$  ( $\alpha_2 = \text{N2—Cu—N41}$ ) and  $110.70(13)^\circ$  ( $\alpha_3 = \text{N21—Cu—N41}$ ). Thus, the Cu—N2 bond is shortened relative to that of a regular trigonal-bipyramidal  $\text{CuN}_5$  chromophore. The angle  $\alpha_3$ , which is opposite to the Cu—N2 bond, is narrower than the ideal angle of  $120^\circ$  by  $9.3^\circ$ , and there is a difference of  $17.9^\circ$  between  $\alpha_1$  and  $\alpha_2$ . According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as trigonal bipyramidal with near  $C_{2v}$  symmetry. According to the values of the angles  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  for the NCS and CN compounds [ $126.62(14)$ ,  $113.19(13)$  and  $120.16(12)^\circ$  and  $131.86(14)$ ,  $124.80(14)$  and  $103.34(11)^\circ$ , respectively], the coordination polyhedra of these complexes can also be best described as trigonal bipyramidal with near  $C_{2v}$  symmetry. The sum of the bond angles in the equatorial plane of the title compound ( $360.0^\circ$ ) indicates coplanarity of the Cu atom with the three equatorial atoms [the deviation of the Cu atom from the N2—N21—N41 plane is  $0.010(3) \text{ \AA}$  towards N11].

Owing to steric forces in the trigonal-bipyramidal polyhedron, the N atoms of the two phen molecules are coordinated both in equatorial and axial positions. The C—C bond distances and C—C—C angles in the phen molecules are quite normal and range from  $1.332(7)$  to  $1.427(7) \text{ \AA}$  and  $115.6(5)$  to  $125.8(5)^\circ$ , respectively. Both phen molecules are almost planar; the largest deviation of atoms from the mean planes is less than  $0.035(6) \text{ \AA}$ . The mean planes of the two phen molecules are inclined at  $112.91(7)^\circ$ .

There are three canonical formulae describing the mode of bonding in the dicyanamide ligand. Inspec-

tion of the bond lengths (Table 2) shows that no canonical formula properly describes the bonding mode in the dicyanamide. Both the  $\text{N}_{\text{cyano}}\equiv\text{C}$  distances [ $\text{N2—C2} = 1.126(6)$  and  $\text{N3—C3} = 1.123(6) \text{ \AA}$ ] and the  $\text{N}_{\text{amide}}=\text{C}$  distances [ $\text{N1—C2} = 1.282(7)$  and  $\text{N1—C3} = 1.282(6) \text{ \AA}$ ] are usual for  $\text{N}\equiv\text{C}$  triple ( $1.153 \text{ \AA}$ ) and  $\text{N}=\text{C}$  double bonds ( $1.270 \text{ \AA}$ ), respectively. The angles  $\text{N1—C2—N2}$  and  $\text{N1—C3—N3}$  [ $172.8(5)$  and  $172.6(5)^\circ$ , respectively] are almost linear while the value of the  $\text{C2—N1—C3}$  angle is  $128.2(4)^\circ$ . The dicyanamide ligand is perfectly planar, the largest deviation of atoms from the mean plane being  $0.003(6) \text{ \AA}$ . According to Golub, Köhler & Skopenko (1986), the bonding mode of the dicyanamide to the Cu atom can be considered as angular [ $\text{C2—N2—Cu} = 159.0(4)^\circ$ ].

The almost planar  $\text{tcm}^-$  anion [the largest deviation of atoms from the mean plane being  $0.015(5) \text{ \AA}$ ] is uncoordinated, probably due to steric repulsion, and serves as a counterion to the  $[\text{Cu}(\text{phen})_2\{\text{N}(\text{CN})_2\}]^+$  cation. The mode of bonding in this anion can be described as a largely delocalized  $\pi$ -bonding system (Golub *et al.*, 1986). According to this assumption, the lengths of the  $\text{C4—CX}$  ( $X = 5, 6, 7$ ) bonds [ $1.374(7)$ ,  $1.395(7)$  and  $1.394(8) \text{ \AA}$ , respectively] are considerably shorter than single  $\text{C}_{sp^2}\text{—C}_{sp}$  bond lengths ( $1.440 \text{ \AA}$ ). However, contrary to this assumption, the  $\text{CX}\equiv\text{NX}$  ( $X = 5, 6, 7$ ) bond lengths [ $1.135(7)$ ,  $1.132(6)$  and  $1.123(6) \text{ \AA}$ , respectively] are slightly shorter than normal  $\text{C}\equiv\text{N}$  triple bond lengths ( $1.153 \text{ \AA}$ ). The angles around the central C4 atom are close to the ideal value of  $120^\circ$ , while the  $\text{C4—CX}\equiv\text{NX}$  ( $X = 5, 6, 7$ ) angles are almost linear.

## Experimental

Crystals were prepared by mixing 1 ml of a 1 M water solution of  $\text{Cu}(\text{NO}_3)_2$  with 20 ml of a 0.1 M methanol solution of phen. A mixture of 10 ml of a 0.2 M water solution of  $\text{KC}(\text{CN})_3$  and 10 ml of a 0.2 M water solution of  $\text{KN}(\text{CN})_2$  was added. Dark green needles of the title complex appeared the following day.

### Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\cdot(\text{C}_4\text{N}_3)$

$M_r = 580.07$

Monoclinic

$P2_1/n$

$a = 10.080(7) \text{ \AA}$

$b = 12.972(7) \text{ \AA}$

$c = 19.874(13) \text{ \AA}$

$\beta = 100.22(6)^\circ$

$V = 2557.4(28) \text{ \AA}^3$

$Z = 4$

$D_x = 1.506 \text{ Mg m}^{-3}$

$D_m = 1.46(1) \text{ Mg m}^{-3}$

$D_m$  measured by flotation in a mixture of  $\text{CCl}_4\text{—CHBr}_3$  and benzene

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 19 reflections

$\theta = 3.82\text{—}11.66^\circ$

$\mu = 0.896 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.7 \times 0.35 \times 0.15 \text{ mm}$

Dark green

## Data collection

Syntex P2 <sub>1</sub> diffractometer	$\theta_{\max} = 25.00^\circ$
$\theta$ - $2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction:	$k = 0 \rightarrow 16$
none	$l = -25 \rightarrow 25$
4505 measured reflections	2 standard reflections
4242 independent reflections	monitored every 98
2477 observed reflections	reflections
[ $I > 2\sigma(I)$ ]	intensity decay: <3%
$R_{\text{int}} = 0.0311$	

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\max} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.0487$	$\Delta\rho_{\max} = 0.444 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1284$	$\Delta\rho_{\min} = -0.474 \text{ e } \text{\AA}^{-3}$
$S = 1.022$	Extinction correction: none
4176 reflections	Atomic scattering factors
434 parameters	from <i>International Tables</i>
All H-atom parameters	for <i>Crystallography</i> (1992,
refined	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2$	6.1.1.4)
+ 0.6875P]	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Cu	0.22641 (5)	0.27679 (4)	0.92376 (3)	0.0487 (2)
N2	0.1063 (4)	0.1559 (3)	0.9241 (2)	0.0659 (11)
C2	0.0718 (4)	0.0732 (5)	0.9196 (2)	0.0634 (13)
N1	0.0462 (5)	-0.0236 (4)	0.9197 (3)	0.113 (2)
N3	-0.1464 (5)	-0.1214 (3)	0.8669 (2)	0.0752 (12)
C3	-0.0598 (5)	-0.0708 (4)	0.8899 (2)	0.0562 (12)
N11	0.0831 (3)	0.3628 (3)	0.8706 (2)	0.0544 (9)
N21	0.2555 (3)	0.4103 (3)	0.9809 (2)	0.0488 (9)
N31	0.3794 (3)	0.2014 (2)	0.9785 (2)	0.0453 (8)
N41	0.3573 (3)	0.2718 (3)	0.8518 (2)	0.0471 (8)
C11	0.0716 (4)	0.4581 (3)	0.8964 (2)	0.0458 (10)
C12	-0.0018 (5)	0.3364 (5)	0.8145 (3)	0.075 (2)
C13	-0.1003 (5)	0.4026 (6)	0.7818 (3)	0.082 (2)
C14	-0.1118 (5)	0.4966 (5)	0.8082 (3)	0.074 (2)
C15	-0.0251 (4)	0.5281 (4)	0.8676 (2)	0.0590 (12)
C16	-0.0308 (6)	0.6253 (4)	0.9005 (3)	0.075 (2)
C21	0.1644 (4)	0.4833 (3)	0.9571 (2)	0.0470 (10)
C22	0.3465 (5)	0.4336 (4)	1.0360 (2)	0.0626 (13)
C23	0.3468 (7)	0.5266 (5)	1.0695 (3)	0.080 (2)
C24	0.2518 (7)	0.5966 (5)	1.0464 (3)	0.077 (2)
C25	0.1563 (5)	0.5785 (3)	0.9880 (2)	0.0595 (12)
C26	0.0553 (6)	0.6486 (4)	0.9577 (3)	0.077 (2)
C31	0.4841 (4)	0.1854 (3)	0.9464 (2)	0.0423 (10)
C32	0.3866 (5)	0.1651 (4)	1.0410 (2)	0.0548 (12)
C33	0.4968 (5)	0.1136 (4)	1.0755 (3)	0.0602 (13)
C34	0.6034 (5)	0.0985 (4)	1.0441 (3)	0.0609 (13)
C35	0.5996 (4)	0.1332 (3)	0.9773 (2)	0.0503 (10)
C36	0.7041 (5)	0.1175 (4)	0.9389 (3)	0.0627 (13)
C41	0.4726 (4)	0.2221 (3)	0.8783 (2)	0.0431 (9)
C42	0.3449 (6)	0.3051 (4)	0.7884 (3)	0.0612 (14)
C43	0.4451 (6)	0.2938 (4)	0.7494 (3)	0.0710 (15)
C44	0.5597 (6)	0.2449 (4)	0.7759 (3)	0.0658 (14)
C45	0.5767 (4)	0.2052 (3)	0.8424 (2)	0.0507 (11)
C46	0.6926 (5)	0.1507 (4)	0.8747 (3)	0.0639 (14)
C4	-0.1316 (5)	0.9089 (4)	0.2813 (2)	0.0620 (12)
C5	-0.1507 (5)	0.8687 (5)	0.3429 (3)	0.0745 (15)
N5	-0.1617 (5)	0.8347 (5)	0.3942 (3)	0.123 (2)
C6	-0.2402 (5)	0.9513 (4)	0.2366 (3)	0.0673 (13)
N6	-0.3286 (5)	0.9857 (4)	0.2005 (3)	0.103 (2)
C7	-0.0028 (6)	0.9029 (4)	0.2651 (3)	0.075 (2)
N7	0.1009 (5)	0.8970 (5)	0.2521 (3)	0.117 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu—N11	1.977 (4)	N3—C3	1.123 (6)
Cu—N31	1.981 (3)	C4—C5	1.374 (7)
Cu—N2	1.982 (4)	C4—C6	1.395 (7)
Cu—N21	2.064 (3)	C4—C7	1.394 (8)
Cu—N41	2.112 (4)	C5—N5	1.135 (7)
N2—C2	1.126 (6)	C6—N6	1.132 (6)
N1—C2	1.282 (7)	C7—N7	1.123 (6)
N1—C3	1.282 (6)		
N11—Cu—N31	175.12 (14)	C2—N2—Cu	159.0 (4)
N11—Cu—N2	93.4 (2)	N2—C2—N1	172.8 (5)
N31—Cu—N2	91.4 (2)	C3—N1—C2	128.2 (4)
N11—Cu—N21	80.79 (15)	N3—C3—N1	172.6 (5)
N31—Cu—N21	95.22 (14)	C5—C4—C7	117.9 (5)
N2—Cu—N21	133.6 (2)	C5—C4—C6	119.9 (5)
N11—Cu—N41	98.04 (14)	C7—C4—C6	122.1 (5)
N31—Cu—N41	80.69 (14)	N5—C5—C4	177.6 (6)
N2—Cu—N41	115.7 (2)	N6—C6—C4	179.7 (5)
N21—Cu—N41	110.70 (13)	N7—C7—C4	179.2 (7)

Intensities were corrected for Lorentz and polarization factors using XP21 (Pavelčík, 1993). The structure was solved by direct methods with *SHELXS86* (Sheldrick, 1985) and subsequent Fourier syntheses using *SHELXL93* (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from the difference Fourier map and refined with free isotropic displacement parameters. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL93*. *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: KA1175). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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