

Low-dimensional compounds containing cyano groups. VII.¹ (Dicyanamido- κN^1)bis(1,10-phenanthroline- $\kappa^2 N, N'$)copper(II) trifluoromethanesulfonate

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The title compound, $[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{CF}_3\text{SO}_3)$, is formed by discrete $[\text{Cu}(\text{phen})_2\{\text{N}(\text{CN})_2\}]^+$ complex cations (phen is 1,10-phenanthroline) and uncoordinated CF_3SO_3^- anions. The Cu centre is five-coordinated in the form of a distorted trigonal bipyramid to two phen molecules and one dicyanamide ligand, which is coordinated through one nitrile N atom in the equatorial plane at a distance of 1.990 (2) Å. The two axial Cu–N distances are similar (mean 1.993 Å) and are substantially shorter than the two equatorial Cu–N bonds (mean 2.125 Å).

Comment

The dicyanamide anion (dca), $[\text{N}(\text{CN})_2]^-$, can be coordinated to a central atom either in a monodentate fashion, through a nitrile or amide N atom, or as a bidentate, tridentate or even tetradentate bridging ligand, with the participation of two or three donor N atoms. Nevertheless, monodentate coordination of dca through an amide N atom is improbable (Kohout *et al.*, 2000), and up to now only one compound with such a dca coordination has been reported (Marshall *et al.*, 2002). On the other hand, the structures of several molecular and ionic compounds with dca coordinated in a monodentate manner through a nitrile N atom have been reported. These compounds either contain six-coordinated central atoms and have the general formula $[\text{ML}_4(\text{dca})_2]$, for example, $[\text{Ni}(\text{teta})(\text{dca})_2]$ (teta is triethylenetetramine; Březina *et al.*, 1999), $[\text{Cu}(\text{phen})_2(\text{dca})_2]$ (phen is 1,10-phenanthroline; Potočňák *et al.*, 1995), $[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{O})_2(\text{dca})_2]$ (NITpPy is the nitronyl nitroxide radical; Dasna *et al.*, 2001) and $[\text{Ni}(4\text{-Meim})_4(\text{dca})_2]$ (4-Meim is 4-methylimidazole; Kožíšek *et al.*,

¹ Part VI: Potočňák, Triščíková & Wagner (2003).

1996), or exhibit five-coordination and have the general formula $[\text{ML}_4(\text{dca})]\text{X}$, for example, $[\text{Cu}(\text{bpy})_2(\text{dca})]\text{BF}_4$, (I) (bpy is 2,2'-bipyridine; Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001), $[\text{Cu}(\text{bpy})_2(\text{dca})]\text{ClO}_4$, (II) (Potočňák *et al.*, 2002), $[\text{Cu}(\text{bpy})_2(\text{dca})][\text{C}(\text{CN})_3]$, (III) (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001), and $[\text{Cu}(\text{phen})_2(\text{dca})][\text{C}(\text{CN})_3]$, (IV) (Potočňák *et al.*, 1996), where L_4 may be one tetradentate, two bidentate or four monodentate ligands, and X is a monoanion.

Understanding the shape of coordination polyhedra (SCP) in the case of five-coordination is one of the current problems in coordination chemistry. With the aim of finding possible reasons for different SCPs in related compounds, we have previously studied the structures of five-coordinated copper(II) complexes of the general formula $[\text{Cu}(L-L)_2\text{X}]\text{Y}$, where L–L is 1,10-phenanthroline or 2,2'-bipyridine, X is an N-donor pseudohalide anion and Y is the tricyanomethanide anion, $[\text{C}(\text{CN})_3]^-$ (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001). The SCP in those compounds with the same counter-anion is a more or less distorted trigonal bipyramid. In more recent work, we have changed our focus from compounds with the same counter-anion to compounds with the same coordinated ligands, having a general formula $[\text{Cu}(L-L)_2(\text{dca})]\text{X}$, where X is a monoanion, *viz.* (I)–(IV) above. We present here the structure of the title compound, $[\text{Cu}(\text{phen})_2(\text{dca})](\text{CF}_3\text{SO}_3)$, (V).

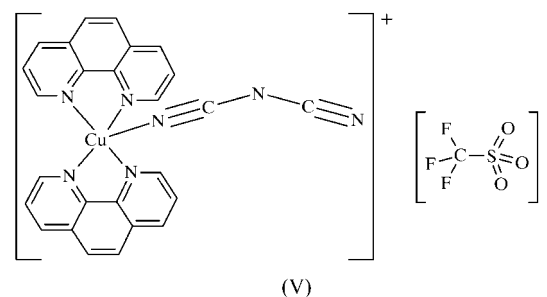


Fig. 1 shows the labelling scheme of one formula unit of (V). The Cu atom is fivefold coordinated by two phen molecules and one $[\text{N}(\text{CN})_2]^-$ ligand (in the equatorial plane). The coordination polyhedron is a distorted trigonal bipyramid, and the CF_3SO_3^- anion, which is in a staggered conformation, does not enter the inner coordination sphere. In the trigonal bipyramid, the two out-of-plane distances (Cu–N1 and Cu–N3) have nearly the same values and are almost collinear (Table 1). The two in-plane distances (Cu–N2 and Cu–N4) are, on average, 0.132 Å longer than the out-of-plane Cu–N distances, which is a feature generally observed for compounds containing the $[\text{Cu}(L-L)_2\text{X}]^+$ cation, where L–L is bpy, and X is Cl^- , Br^- or I^- (O'Sullivan *et al.*, 1999); L–L is phen, and X is Cl^- (Murphy *et al.*, 1998), Br^- (Murphy, Nagle *et al.*, 1997) or H_2O (Murphy, Murphy *et al.*, 1997); and L–L is phen or bpy, and X is a pseudohalide monoanion (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001). The third in-plane distance (Cu–N5; atom N5 is from dca) is shorter than the other two in-plane distances and is comparable to the out-of-plane distances. The same trends in bond distances are

observed in $[\text{Cu}(\text{bpy})_2(\text{dca})]X$, where X is BF_4^- (I) (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001), or ClO_4^- (II) (Potočňák *et al.*, 2002), and in the related compound $[\text{Cu}(\text{phen})_2(\text{dca})][\text{C}(\text{CN})_3]$ (IV) (Potočňák *et al.*, 1996). However, for $[\text{Cu}(\text{bpy})_2(\text{dca})]X$ where the non-coordinating out-of-sphere X anion is $[\text{C}(\text{CN})_3]^-$ (III) (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001), the Cu—N5 bond is the shortest Cu—N bond. Table 2 gives details of these comparisons.

The out-of-plane angles in (V) lie in the range 80.40 (9)– 97.22 (8)°, which is similar to the range of values observed in compounds (I)–(IV). The bond angles in the equatorial plane of (V) differ considerably from the ideal trigonal angle of 120° , with one wide angle of 135.28 (9)° ($\alpha_1 = \text{N5—Cu—N4}$), one normal angle of 121.20 (10)° ($\alpha_2 = \text{N5—Cu—N2}$) and one narrow angle of 103.51 (8)° ($\alpha_3 = \text{N4—Cu—N2}$). Corresponding values for (I)–(IV) are given in Table 2. Thus, the α_3 angle, which is opposite the Cu—N5 bond, is 16.49° narrower than the ideal angle of 120° , and there is a difference of 14.08° between α_1 and α_2 .

According to the criteria of Harrison & Hathaway (1980), based on the values of the three equatorial angles and their differences, the coordination polyhedron around the Cu atom can be best described as trigonal-bipyramidal with approximate C_{2v} symmetry, which is similar to the conformation of (IV). On the other hand, according to the values of the α_1 , α_2 and α_3 angles, the coordination polyhedra of (I)–(III) can be best described as distorted trigonal-bipyramidal, with a distortion toward square-pyramidal. These SCPs are in accordance with the values of the τ parameter [Table 2; the τ parameter is 100 for an ideal trigonal bipyramid and 0 for an ideal square pyramid (Addison *et al.*, 1984)]. This difference in the SCP of (IV) and (V) on the one hand and of (I)–(III) on

the other can be explained by the lower rigidity of the bpy ligand compared with the rigidity of the phen ligand. While the two outer pyridine rings in a phen molecule are connected by a phenyl ring, making the whole molecule planar, the two pyridine rings in a bpy molecule can rotate around their common C—C single bond.

Both phenanthroline molecules in (V) are almost planar [the largest deviation from the mean plane is 0.073 (3) Å for atom C24], and the bond distances and angles in these molecules are as expected. The dihedral angle between the two phenanthroline ligands is 83.59 (3)°.

There are three canonical formulae describing the mode of bonding in a dicyanamide ligand, including single and double $\text{N}_{\text{amide}}\text{—C}$ bonds, and double and triple $\text{N}_{\text{cyano}}\text{—C}$ bonds (Golub *et al.*, 1986). Inspection of the bond lengths (Table 1) shows that no canonical formula properly describes the bonding mode in this particular dicyanamide. The $\text{N}_{\text{cyano}}\equiv\text{C}$ and $\text{N}_{\text{amide}}=\text{C}$ distances are typical of $\text{N}\equiv\text{C}$ triple (1.15 Å) and $\text{N}=\text{C}$ double bonds (1.27 Å), respectively. The N6—C1—N5 and N6—C2—N7 angles are almost linear, while the value of the C1—N6—C2 angle is close to 120° . The dicyanamide ligand is nearly planar, the largest deviation of an atom from the mean plane being 0.011 (3) Å. The coordination of the dicyanamide through the N_{cyano} atom results in an angular arrangement [$\text{C1—N5—Cu} = 151.6$ (2)°].

Experimental

Crystals of (V) were prepared by mixing an aqueous solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.1 M, 5 ml) with an ethanol solution of phen (0.1 M, 10 ml). To the resulting green solution, an aqueous solution of $\text{NaN}(\text{CN})_2$ (0.1 M, 5 ml) was added (all solutions were warmed before mixing). Green crystals of the title complex appeared the next day, and these crystals were filtered off and dried in air.

Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{CF}_3\text{SO}_3)$
 $M_r = 639.07$
 Triclinic, $P\bar{1}$
 $a = 8.6026$ (19) Å
 $b = 9.957$ (2) Å
 $c = 15.664$ (4) Å
 $\alpha = 79.05$ (3)°
 $\beta = 87.01$ (3)°
 $\gamma = 79.64$ (3)°
 $V = 1295.6$ (5) Å³

$Z = 2$
 $D_x = 1.638$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 1.7\text{--}26.1^\circ$
 $\mu = 0.99$ mm⁻¹
 $T = 220$ (1) K
 Prism, green
 $0.33 \times 0.12 \times 0.11$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: numerical
 (FACE in IPDS; Stoe & Cie, 1999)
 $T_{\text{min}} = 0.793$, $T_{\text{max}} = 0.913$
 10 138 measured reflections

4678 independent reflections
 3840 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.100$
 $S = 1.06$
 4678 reflections
 379 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.6424P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

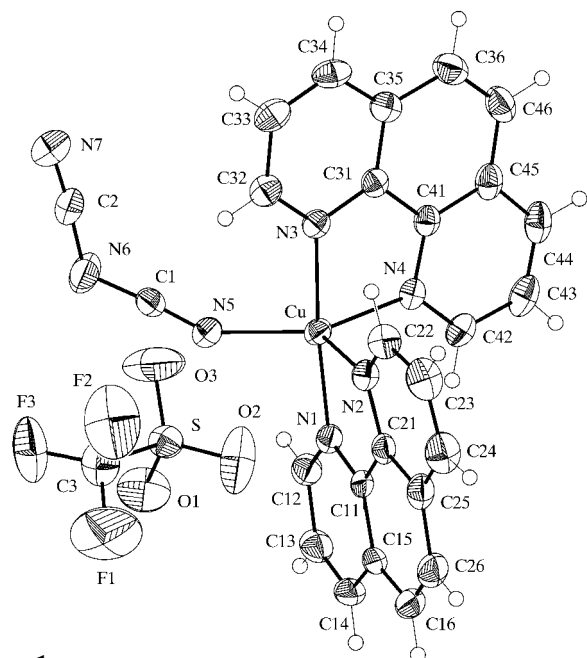


Figure 1

A view of the structure of (V), showing the atom-labelling scheme. Displacement ellipsoids have been drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 1

Selected geometric parameters (Å, °).

Cu—N1	1.990 (2)	N6—C1	1.294 (4)
Cu—N5	1.990 (2)	N6—C2	1.316 (4)
Cu—N3	1.995 (2)	C1—N5	1.145 (3)
Cu—N4	2.108 (2)	N7—C2	1.145 (4)
Cu—N2	2.141 (2)		
N1—Cu—N5	93.14 (10)	N5—Cu—N2	121.20 (10)
N1—Cu—N3	174.98 (9)	N3—Cu—N2	97.22 (8)
N5—Cu—N3	91.87 (10)	N4—Cu—N2	103.51 (8)
N1—Cu—N4	95.12 (9)	C1—N6—C2	119.2 (3)
N5—Cu—N4	135.28 (9)	N5—C1—N6	174.3 (3)
N3—Cu—N4	81.09 (9)	C1—N5—Cu	151.6 (2)
N1—Cu—N2	80.40 (9)	N7—C2—N6	174.4 (3)

Table 2

 A comparison of geometric parameters (Å, °) for some [CuL₄(dca)]⁺ species.

Parameter	(I)	(II)	(III)	(IV)	(V)
Cu—N1†	2.006 (3)	2.0024 (17)	1.998 (4)	1.981 (3)	1.990 (2)
Cu—N3	1.998 (3)	1.9916 (17)	1.975 (4)	1.977 (4)	1.995 (2)
Cu—N2	2.142 (3)	2.1456 (19)	2.116 (4)	2.112 (4)	2.141 (2)
Cu—N4	2.043 (3)	2.0395 (19)	2.027 (4)	2.064 (3)	2.108 (2)
Cu—N5	2.015 (3)	1.995 (2)	1.973 (5)	1.982 (4)	1.990 (2)
N1—Cu—N3	177.52 (12)	177.16 (9)	175.3 (2)	175.12 (14)	174.98 (9)
α ₁	145.00 (13)	146.66 (8)	140.0 (2)	133.6 (2)	135.28 (9)
α ₂	108.54 (12)	108.46 (8)	112.4 (2)	115.7 (2)	121.20 (10)
α ₃	106.45 (11)	104.87 (8)	107.6 (2)	110.70 (13)	103.51 (8)
τ	54.2	50.8	58.8	69.2	66.2

Notes: (I) is [Cu(bpy)₂(dca)]BF₄ (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001), (II) is [Cu(bpy)₂(dca)]ClO₄ (Potočňák *et al.*, 2002), (III) is [Cu(bpy)₂(dca)] [C(CN)₃] (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001), (IV) is [Cu(phen)₂(dca)] [C(CN)₃] (Potočňák *et al.*, 1996) and (V) is [Cu(phen)₂(dca)] (CF₃SO₃) (this work). † Numbering schemes have been standardized as for (V).

All H-atom positions were calculated using an appropriate riding model, with U_{iso} values of 1.2 U_{eq} of the parent C atom. Geometric analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL97* (Sheldrick, 1997).

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1060). Services for accessing these data are described at the back of the journal.

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