

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

Milan Burčák,^a Ivan Potočňák,^{a*} Peter Baran^b and Lothar Jäger^c

^aDepartment of Inorganic Chemistry, Faculty of Science, P.J. Šafárik University, Moyzesova 11, SK-041 54 Košice, Slovakia, ^bDepartment of Chemistry, University of Puerto Rico, Río Piedras Campus, PO Box 23346, San Juan, PR 00931-3346, Puerto Rico, and ^cInstitute of Inorganic Chemistry, Martin-Luther-University, Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany
Correspondence e-mail: potocnak@kosice.upjs.sk

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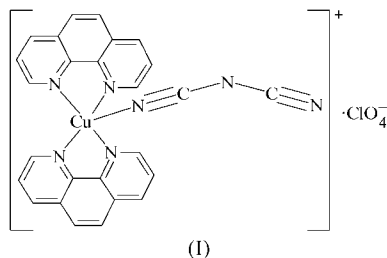
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The title compound, $[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{ClO}_4$, represents a relatively rare class of compounds with dicyanamide coordinated in a monodentate manner. The structure is formed by the $[\text{Cu}\{\text{N}(\text{CN})_2(\text{phen})_2\}]^+$ complex cation (phen is 1,10-phenanthroline) and an uncoordinated ClO_4^- anion. The Cu atom is five-coordinate, with a slightly distorted trigonal-bipyramidal environment. The dicyanamide ligand is coordinated through one nitrile N atom in the equatorial plane, at a distance of 2.033 (6) Å from the metal. The two axial Cu–N distances are similar [mean 1.999 (4) Å] and are substantially shorter than the remaining two equatorial Cu–N bonds [mean 2.087 (1) Å].

Comment

The dicyanamide anion (dca), $[\text{N}(\text{CN})_2]^-$, can coordinate either as a monodentate ligand through the nitrile or amide N atom, or as a bi-, tri-, tetra- or even pentadentate bridging ligand with the participation of two or three donor N atoms. Nevertheless, monodentate coordination of dca through the amide N atom is rather improbable (Kohout *et al.*, 2000) and



to date only two compounds with this type of dca coordination are known (Marshall *et al.*, 2002; Montgomery *et al.*, 1993). On

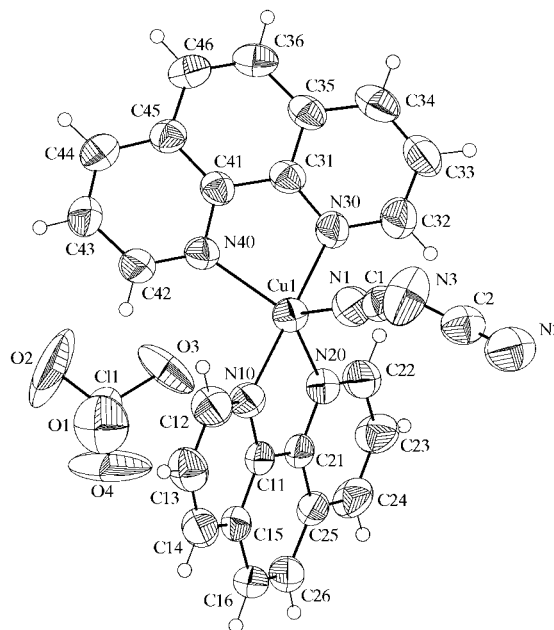


Figure 1

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Only one position of the disordered perchlorate anion is shown.

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-coordinate central atoms and are of the general formula $[\text{M}(\text{dca})_2\text{L}_4]$, e.g. $[\text{Ni}(\text{dca})_2(\text{teta})]$ (teta is triethylenetetramine; Březina *et al.*, 1999), $[\text{Cu}(\text{dca})_2(\text{phen})_2]$ (phen is 1,10-phenanthroline; Potočňák *et al.*, 1995), $[\text{Cu}(\text{dca})_2(\text{NITpPy})_2(\text{H}_2\text{O})_2]$ (NITpPy is the nitronyl nitroxide radical; Dasna *et al.*, 2001) and $[\text{Ni}(\text{dca})_2(4\text{-Meim})_4]$ (4-Meim is 4-methylimidazole; Kožíšek *et al.*, 1996), or exhibit five-coordination and have the general formula $[\text{M}(\text{dca})\text{L}_4]\text{X}$, e.g. $[\text{Cu}(\text{dca})(\text{bpy})_2]\text{BF}_4$ (bpy is 2,2'-bipyridine; Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001) and $[\text{Cu}(\text{dca})(\text{phen})_2][\text{C}(\text{CN})_3]$ (Potočňák *et al.*, 1996), in which L_4 may be one tetradentate, two bidentate or four monodentate ligands, and X is a monoanion.

Understanding the shape of the coordination polyhedra (SCP) in the case of five-coordination is one of the current problems in coordination chemistry. With the aim of elucidating the factors which determine the SCP in related compounds, we have previously studied structures of five-coordinate copper(II) complexes of the general formula $[\text{CuX}(\text{L})_2][\text{C}(\text{CN})_3]$, where L is phen or bpy and X is an N-donor pseudohalide anion (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001). More or less distorted trigonal bipyramids were found in those compounds. Recently, we have focused on compounds with the same inner coordination sphere and studied the influence of the counter-anion in complexes with the general formula $[\text{Cu}(\text{dca})(\text{L})_2]\text{Y}$, where L is phen and Y is CF_3SO_3^- , (II), or $\text{C}(\text{CN})_3^-$, (III), or where L is bpy and Y is ClO_4^- , (IV), CF_3SO_3^- , (V), $\text{C}(\text{CN})_3^-$, (VI) or BF_4^- , (VII)

(Potočňák *et al.*, 2003). This paper is a continuation of that work and we present here the structure of $[\text{Cu}(\text{dca})(\text{phen})_2]\text{ClO}_4$ (I).

Fig. 1 shows the labelling scheme of one formula unit of (I). The Cu atom is pentacoordinated by two phen molecules and one $[\text{N}(\text{CN})_2]^-$ ligand. The coordination polyhedron is a distorted trigonal bipyramid (TBP). The two axial distances involving phen (Cu1–N10 and Cu1–N30) are almost equal and are essentially collinear. The two equatorial distances (Cu1–N20 and Cu1–N40) are of the same length (within 1σ) and their average is 0.088 \AA longer than the axial Cu–N distances, which is a feature generally observed for compounds with the $[\text{Cu}X(L)_2]$ cation, where L is bpy and X is Cl^- , Br^- or I^- (O'Sullivan *et al.*, 1999), where 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), or where L is phen or bpy and X is a pseudohalide(1-) anion (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001). The third equatorial distance, Cu1–N1 [$2.033(6) \text{ \AA}$, N atom from dca], is shorter than the other two but is 0.035 \AA longer than the two axial bonds. This differs from compounds (II)–(VII), in which the Cu–N_{dca} bond length is comparable with the two axial bonds and in some cases is the shortest Cu–N bond. Table 2 gives details for the purpose of comparison.

The $N_{\text{ax}}\text{—Cu—}N_{\text{eq}}$ angles span the range $80.74(18)$ – $99.04(18)^\circ$ in (I), as they do in (II)–(VII). The $N_{\text{eq}}\text{—Cu—}N_{\text{eq}}$ bond angles in (I) are not ideal trigonal angles of 120° ; one of them is slightly greater [$N40\text{—Cu1—}N20$ (α_3) = $126.40(17)^\circ$], one has a normal value [$N1\text{—Cu1—}N40$ (α_1) = $118.41(19)^\circ$] and one is slightly smaller [$N1\text{—Cu1—}N20$ (α_2) = $115.19(19)^\circ$]. The corresponding values for (II)–(VII) are given in Table 2. For complexes (II)–(VII), α_1 is the second largest angle in the Cu coordination polyhedron, while in (I), the second largest angle is α_3 . In a putative square-pyramidal distortion of the TBP arrangement of donor atoms, atom N20 from phen or bpy would become an apical atom in (II)–(VII), but in (I), the apical atom would be N1 from dca. Because the differences between the observed and ideal values are not great in (I), the SCP around copper can be considered as TBP, with atom Cu1 lying in the trigonal plane. This is in accord with the value of the τ parameter [Table 2; $\tau = 100$ for an ideal TBP or 0 for an ideal square pyramid (SP); Addison *et al.*, 1984]. We have shown in our previous work (Potočňák & Burčák, 2003) that the τ parameter does not always describe the SCP correctly. Therefore, besides τ , another more reliable criterion is presented in Table 2 to describe the actual SCP in five-coordinate compounds, namely the sum of the angle deviations for a TBP, $\Sigma(\text{TBP})$ (Holmes & Deiters, 1977). According to this criterion, a larger value of $\Sigma(\text{TBP})$ represents a greater deviation of the SCP from the ideal TBP. The data in Table 2 show that compounds (I)–(III) (all containing phen ligands), achieve lower $\Sigma(\text{TBP})$ values than compounds (IV)–(VII), which contain bpy ligands, which corresponds to a greater distortion of the TBP of the latter group compared with the former. We believe that the observed difference can be explained by the lower rigidity of bpy compared with phen. While the two outer pyridine rings in a phen molecule are

connected by a phenyl ring, making the whole molecule planar and rigid, the two pyridine rings in a bpy molecule can rotate around their common C–C single bond. Our results indicate that compounds with rigid chelating ligands prefer a TBP SCP, while those with more flexible chelating ligands have an SCP more distorted towards square pyramidal.

Both phen moieties in (I) are nearly planar [the largest deviation from the mean plane is $0.067(6) \text{ \AA}$ for atom C14] and exhibit the expected bond lengths and angles. The two phen ligands form a dihedral angle of $54.48(8)^\circ$.

There are three canonical forms describing the mode of bonding in the dicyanamide ligand, including single and double $N_{\text{amide}}\text{—C}$ bonds, and double and triple $N_{\text{cyano}}\text{—C}$ bonds (Golub *et al.*, 1986). Inspection of the bond lengths in (I) (Table 1) shows that no canonical form properly describes the bonding mode in this particular dicyanamide. The $N_{\text{amide}}\text{=C}$ distances (N3=C1 and N3=C2) are typical for N=C double bonds (1.27 \AA ; Jolly, 1991), but the $N_{\text{cyano}}\text{=C}$ distances (C1=N1 and C2=N2) are shorter than typical N=C triple bonds (1.15 \AA ; Jolly, 1991). The N3–C1–N1 and N3–C2–N2 angles are almost linear, while the C1–N3–C2 angle is close to 120° . The dicyanamide ligand is nearly planar, with the largest deviation from the mean plane being $0.021(7) \text{ \AA}$ for atom C2. According to Golub *et al.* (1986), the bonding mode of the dicyanamide to the Cu atom can be considered as linear [C1–N1–Cu1 = $173.1(6)^\circ$].

The ClO_4^- anion does not enter the inner coordination sphere of the Cu atom in (I). Atoms O2, O3 and O4 are disordered over two positions, but their displacement ellipsoids are still quite large, indicating possible rotational disorder, with the rotation axis passing through atoms C11 and O1.

Besides ionic forces, the structure of (I) is stabilized by weak C–H...X hydrogen bonds (X is O or N); those with C–H...X angles greater than 120° and H...X distances less than 2.6 \AA are given in Table 3. Further stabilization may come from possible $\pi\text{--}\pi$ interactions between stacked phen entities. There is a stacking interaction involving one of the phen ligands [that containing atoms N30 and N40 and its symmetry relative at $(-x, 1-y, 1-z)$], with the shortest distance of $3.514(7) \text{ \AA}$ being between atoms C36 and C31($-x, 1-y, 1-z$). There is another stacking interaction involving the phen ligand containing atoms N10 and N20, and that containing N30 and N40, with the latter at symmetry position $(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$. The shortest distance of $3.314(7) \text{ \AA}$ involves atoms C26 and C34($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$). Because the angle between the mean planes of these two phen ligands is $13.2(6)^\circ$, the other C...C($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$) distances are longer and, moreover, this second interaction seems to have less overlap than the first.

Experimental

Crystals of (I) were prepared by mixing a solution of $\text{Cu}(\text{ClO}_4)_2$ (5 ml, 0.1 M in dimethylformamide) with a solution of phen (10 ml, 0.1 M in ethanol). To the resulting green solution was added a solution of $\text{NaN}(\text{CN})_2$ (5 ml, 0.1 M in water) (all solutions were warmed

before mixing). Green crystals of (I) appeared after a week. The crystals were filtered off and dried in air.

Crystal data

[Cu(C₂N₃)(C₁₂H₈N₂)₂]ClO₄
M_r = 589.45
 Orthorhombic, *Pbca*
a = 14.9903 (17) Å
b = 15.3555 (18) Å
c = 21.022 (3) Å
V = 4838.8 (10) Å³
Z = 8
D_x = 1.618 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 878 reflections
 θ = 2.7–16.8°
 μ = 1.06 mm⁻¹
T = 300 (2) K
 Prism, green
 0.10 × 0.05 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*XPREP*; Sheldrick, 1990)
T_{min} = 0.820, *T_{max}* = 0.924
 23 973 measured reflections

4527 independent reflections
 2150 reflections with *I* > 2σ(*I*)
R_{int} = 0.089
 θ_{max} = 25.6°
h = -16 → 18
k = -17 → 18
l = -25 → 24

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.057
wR (*F*²) = 0.169
S = 0.99
 4527 reflections
 381 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0009 (2)

Table 1

Selected geometric parameters (Å, °).

Cu1—N30	1.996 (5)	C1—N1	1.088 (7)
Cu1—N10	2.001 (5)	C1—N3	1.282 (8)
Cu1—N1	2.033 (6)	C2—N2	1.130 (8)
Cu1—N40	2.086 (4)	C2—N3	1.290 (9)
Cu1—N20	2.087 (5)		
N30—Cu1—N10	179.14 (19)	N10—Cu1—N20	80.74 (18)
N30—Cu1—N1	90.4 (2)	N1—Cu1—N20	115.19 (19)
N10—Cu1—N1	90.4 (2)	N40—Cu1—N20	126.40 (17)
N30—Cu1—N40	80.82 (18)	N1—C1—N3	172.7 (7)
N10—Cu1—N40	98.64 (18)	C1—N1—Cu1	173.1 (6)
N1—Cu1—N40	118.41 (19)	N2—C2—N3	172.2 (8)
N30—Cu1—N20	99.04 (18)	C1—N3—C2	123.6 (6)

Table 2

Comparison of molecular geometry parameters (Å, °) for some [Cu(dca)L₄]⁺ species.

Numbering schemes have been standardized as for (I). α₁, α₂, α₃, τ and Σ(TBP) are defined in the *Comment* text.

Parameter	(I)	(II)	(III)	(IV)	(Va)†	(Vb)	(VI)	(VII)
Cu1—N10	2.001 (5)	1.990 (2)	1.981 (3)	2.0024 (17)	1.999 (3)	2.013 (3)	1.998 (4)	2.006 (3)
Cu1—N30	1.996 (5)	1.995 (2)	1.977 (4)	1.9916 (17)	2.004 (3)	2.010 (3)	1.975 (4)	1.998 (3)
Cu1—N20	2.087 (5)	2.141 (2)	2.112 (4)	2.1456 (19)	2.128 (3)	2.059 (3)	2.116 (4)	2.142 (3)
Cu1—N40	2.086 (4)	2.108 (2)	2.064 (3)	2.0395 (19)	2.050 (3)	2.137 (3)	2.027 (4)	2.043 (3)
Cu1—N1	2.033 (6)	1.990 (2)	1.982 (4)	1.995 (2)	2.001 (3)	1.988 (4)	1.973 (5)	2.015 (3)
N10—Cu1—N30	179.14 (19)	174.98 (9)	175.12 (14)	177.16 (9)	176.62 (12)	174.29 (13)	175.3 (2)	177.52 (12)
α ₁	118.41 (19)	135.28 (9)	133.6 (2)	146.66 (8)	136.22 (14)	138.08 (14)	140.0 (2)	145.00 (13)
α ₂	115.19 (1)	121.20 (10)	115.7 (2)	108.46 (8)	106.52 (13)	116.45 (14)	112.4 (2)	108.54 (12)
α ₃	126.40 (1)	103.51 (8)	110.70 (13)	104.87 (8)	117.25 (11)	105.45 (11)	107.6 (2)	106.45 (11)
τ	87.9	66.2	69.2	50.8	67.3	60.4	58.8	54.2
Σ(TBP)	50.6	73.9	68.7	97.3	76.3	82.3	85.6	93.2

† (Va) and (Vb) denote two different polyhedra in (V). Notes: (I) is [Cu(dca)(phen)₂]ClO₄ (this work), (II) is [Cu(dca)(phen)₂]CF₃SO₃ (Potočňák *et al.*, 2003), (III) is [Cu(dca)(phen)₂][C(CN)₃] (Potočňák *et al.*, 1996), (IV) is [Cu(dca)(bpy)₂]ClO₄ (Potočňák *et al.*, 2002), (Va) and (Vb) are [Cu(dca)(bpy)₂]CF₃SO₃ (Burčák *et al.*, 2004), (VI) is [Cu(dca)(bpy)₂][C(CN)₃] (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001) and (VII) is [Cu(dca)(bpy)₂]BF₄ (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001).

Table 3

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C43—H43...O4 ⁱ	0.93	2.53	3.17 (2)	126
C26—H26...O1 ⁱⁱ	0.93	2.58	3.498 (8)	171
C12—H12...N3 ⁱⁱⁱ	0.93	2.44	3.289 (9)	153
C13—H13...O2 ^{iv}	0.93	2.45	3.35 (2)	165
C13—H13...O7 ^v	0.93	2.47	3.37 (3)	164
C14—H14...O4 ^v	0.93	2.51	3.32 (2)	146

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

All H-atom positions were calculated and then refined using a riding model, with *U_{iso}*(H) = 1.2*U_{eq}*(C). Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL97* (Sheldrick, 1997).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL* (Bruker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1074). Services for accessing these data are described at the back of the journal.

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