

Low-dimensional compounds containing cyano groups. XVI. (Dicyanamido- κN^1)bis(1,10-phenanthroline- $\kappa^2 N, N'$)copper(II) tetrafluoridoborate¹

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Received 15 February 2008

Accepted 3 March 2008

Online 15 March 2008

The title compound, $[\text{Cu}\{\text{N}(\text{CN})_2\}(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{BF}_4$, was prepared as part of our study of the shape of coordination polyhedra in five-coordinated copper(II) complexes. Single-crystal X-ray analysis reveals that the structure consists of $[\text{Cu}\{\text{N}(\text{CN})_2\}(\text{phen})_2]^+$ cations (phen is 1,10-phenanthroline) and BF_4^- anions. The Cu centre is five-coordinated in a distorted trigonal bipyramidal manner by four N atoms of two phen ligands and one N atom of a dicyanamide anion, which is coordinated in the equatorial plane at a distance of 1.996 (2) Å. The two axial Cu—N_{phen} distances have similar values [average 1.994 (6) Å] and are shorter than the two equatorial Cu—N_{phen} bonds [average 2.09 (6) Å]. This work demonstrates the effect of ligand rigidity on the shape of coordination polyhedra in five-coordinated copper(II) complexes.

Comment

Understanding the shape of coordination polyhedra (SCP) in the case of five-coordination is one of the current problems in coordination chemistry (Murphy & Hathaway, 2003). The molecular structures of five-coordinated copper(II) complexes range from regular trigonal bipyramidal to regular tetragonal-pyramidal, with most complexes falling between these two stereochemistries. In the majority of $[\text{CuX}(L)_2]Y$ complexes, where L is a bidentate chelating ligand and X and Y are singly-charged anions, the differences in stereochemistry may be associated with the differences in the ligands present (Youngme *et al.*, 2007). A number of different structural approaches have been used in the past to describe the

geometries of these compounds (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001, and references therein). In our search for possible reasons for different SCP in related compounds, we have previously studied the structures of five-coordinated copper(II) coordination compounds of the general formula $[\text{Cu}(\text{dca})(L)_2]Y$, where L is 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy), dca is the dicyanamide anion, $\text{N}(\text{CN})_2^-$, and Y is a singly-charged anion (Potočňák *et al.*, 2005). The SCP in these compounds is more or less distorted trigonal bipyramidal. However, we have found that the SCP is more distorted in compounds with bpy molecules than in those involving phen ligands. We suppose that the reason could be the difference in rigidity between highly rigid phen and less rigid bpy ligands. The title compound, $[\text{Cu}(\text{dca})(\text{phen})_2]\text{BF}_4$, (I), has been prepared as the next example within the framework of our ongoing studies. We present here the structure of (I) and compare it with the previously reported compound $[\text{Cu}(\text{dca})(\text{bpy})_2]\text{BF}_4$, (II) (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001).

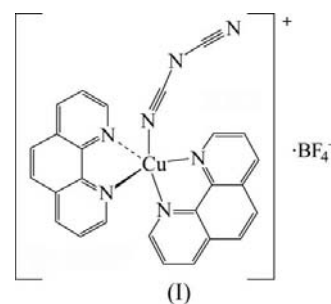


Fig. 1 shows the structure and labelling scheme of one formula unit of (I). The Cu atom is coordinated by two bidentate chelating phen ligands in two axial [average Cu—N =

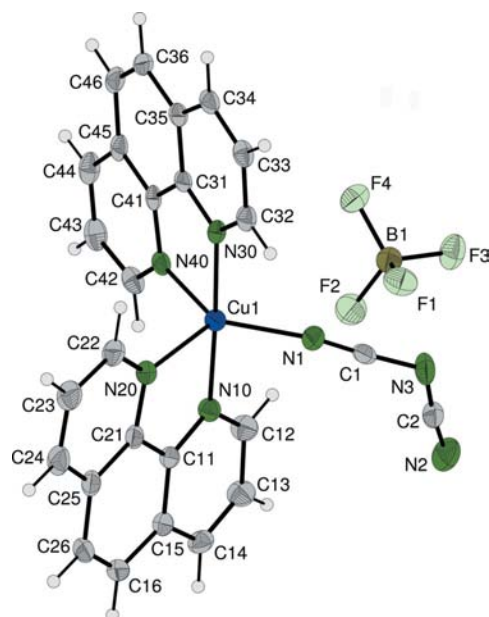


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

¹ Part XV: Potočňák *et al.* (2008).

1.994 (6) Å] and two equatorial positions [average Cu–N = 2.09 (6) Å], whereas one terminal N atom of the dca ligand occupies the third equatorial position of a deformed trigonal bipyramid [Cu1–N1 = 1.996 (2) Å]. The BF₄[−] anion does not enter the inner coordination sphere. The same coordination of bpy and dca ligands and similar corresponding bond distances were observed in (II).

Although the SCP around the Cu atoms in (I) and (II) are quite similar, they still differ in some details. The out-of-plane angles in (I) lie within the range 80.29 (9)–97.52 (9)°, similar to those observed in (II). The angles in the equatorial planes of (I) and (II) differ considerably from the ideal trigonal angle of 120°. If, according to the criteria of Harrison & Hathaway (1980), the angles N1–Cu1–N20, N1–Cu1–N40 and N20–Cu1–N40 are labelled α_1 , α_2 and α_3 , respectively, then the small angle α_3 [109.41 (9)°], which is opposite the Cu1–N1 bond (N1 from dca), and the rather large difference of 22.67° between α_1 and α_2 classify the coordination polyhedron around the Cu atom in (I) as trigonal bipyramidal, with a distortion towards square pyramidal. Atoms N10, N30 and N40 of the phen ligands and atom N1 of the dca ligand represent the base of the distorted square pyramid thus formed [average Cu–N = 2.01 (3) Å], whereas atom N20, owing to the Jahn–Teller effect, occupies the axial position at a longer distance [2.134 (2) Å]. The same result can be obtained, of course, when using the τ parameter of Addison *et al.* (1984) as the criterion, the value being 67.7 here (the τ parameter is 100 for an ideal trigonal bipyramid and 0 for an ideal square pyramid). For (II), the smaller value of the α_3 angle [106.44 (11)°], and the larger difference of 36.45° between α_1 and α_2 , indicate a greater distortion of the trigonal bipyramid towards a square pyramid compared with (I). The smaller value of the τ parameter (54.2) confirms this increasing distortion. This may be seen as a confirmation of our hypothesis on the dependence of the SCP on the different rigidity of the chelating *L* ligands employed.

There are three canonical formulae describing the bonding mode in a dicyanamide ligand (Golub *et al.*, 1986). Inspection of the bond lengths (Table 1) shows that the bonds associated with atom C1 are a little shorter than the bonds around atom C2. Nevertheless, both N≡C (C1≡N1 and C2≡N2) bond lengths in (I) are normal for an N≡C triple bond. On the other hand, the C2–N3 bond length is only slightly longer than a single bond between an N atom and an *sp*-hybridized C atom (1.31 Å Greenwood & Earnshaw, 1998), whereas the C1–N3 bond length is only slightly longer than a double bond between an N atom and an *sp*-hybridized C atom (1.28 Å Greenwood & Earnshaw, 1998). Therefore, no canonical formula correctly describes the bonding mode in the dicyanamide ligand in (I). In accordance with Golub *et al.* (1986), the bonding mode of the dicyanamide ligand to the Cu atom can be considered as angular [C1–N1–Cu1 = 144.2 (2)°].

The BF₄[−] anion remains uncoordinated, with B–F bond lengths and F–B–F angles typical for tetrafluoridoborates (Cambridge Structural Database, Version 5.29 of November 2007, 6734 hits; Allen, 2002). The anion is involved in numerous weak C–H⋯F hydrogen bonds which contribute

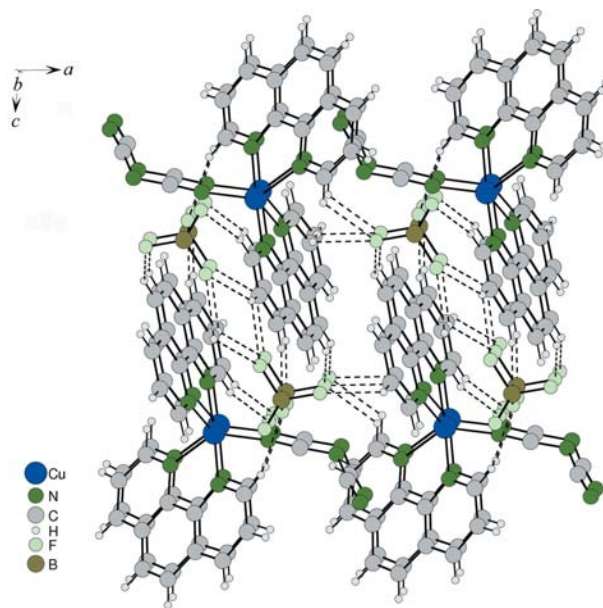


Figure 2
The hydrogen bonds (dashed lines) connecting the cations and anions of (I) into layers parallel to the (001) plane.

to the stabilization of the crystal structure of (I). Those with a C–H⋯F angle greater than 120° and an H⋯F distance less than 2.6 Å are given in Table 2. Through these hydrogen bonds, cations and anions are interconnected to form layers along the (001) plane, as shown in Fig. 2.

Further stabilization of the structure may come from possible face-to-face π – π interactions between stacked phen molecules. There is a stacking interaction involving one benzene and one pyridine ring of the phen ligands from neighbouring layers [that containing atoms N30 and N40 and its symmetry-related layer at (1 – *x*, 1 – *y*, 1 – *z*)], with a centroid-to-centroid distance of 3.609 (4) Å. Another stacking interaction involves only the benzene rings of the phen ligands from the same layer containing atoms N10 and N20 and its symmetry-related layer at (1 – *x*, 1 – *y*, –*z*), with a centroid-to-centroid distance of 3.498 (4) Å.

Experimental

Crystals of (I) were prepared by mixing a 0.1 *M* aqueous solution of Cu(BF₄)₂ (5 ml) with a 0.1 *M* methanolic solution of phen (10 ml). To the resulting green solution, a 0.1 *M* aqueous solution of NaN(CN)₂ (5 ml) was added (all solutions were warmed before mixing). Green crystals of the title complex appeared after 3 d. The crystals were filtered off and dried in air.

Crystal data

[Cu(C₂N₃)(C₁₂H₈N₂)₂]₂BF₄

M_r = 576.81

Triclinic, *P* $\bar{1}$

a = 8.0601 (8) Å

b = 9.2246 (9) Å

c = 16.4286 (15) Å

α = 92.344 (7)°

β = 96.656 (8)°

γ = 103.097 (8)°

V = 1178.8 (2) Å³

Z = 2

Mo *K* α radiation

μ = 0.99 mm^{−1}

T = 110 (2) K

0.40 × 0.35 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with CCD detector	8578 measured reflections 4116 independent reflections 3555 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.693$, $T_{\text{max}} = 0.755$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	352 parameters
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.98 \text{ e } \text{Å}^{-3}$
4116 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{Å}^{-3}$

All H-atom positions were calculated using the appropriate riding model, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The maximum and minimum residual electron-density peaks are located 0.97 and 0.93 Å, respectively, from the Cu atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *PARST* (Nardelli, 1983) and *SHELXL97*.

This work was supported by the Slovak Grant Agency VEGA (grant No. 1/0079/08), APVT (grant No. 20-005204) and the Ministry of Education, Youth and Sports of the Czech Republic (grant No. MSM6198959218).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3073). Services for accessing these data are described at the back of the journal.

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Table 1

Selected geometric parameters (Å, °).

Cu1—N30	1.989 (2)	N1—C1	1.150 (4)
Cu1—N10	1.998 (2)	C1—N3	1.288 (4)
Cu1—N1	1.996 (2)	N3—C2	1.318 (4)
Cu1—N40	2.053 (2)	C2—N2	1.155 (4)
Cu1—N20	2.134 (2)		
N30—Cu1—N10	177.26 (9)	N10—Cu1—N20	80.29 (9)
N30—Cu1—N1	92.28 (9)	N1—Cu1—N20	113.96 (10)
N10—Cu1—N1	89.94 (10)	N40—Cu1—N20	109.41 (9)
N30—Cu1—N40	81.96 (9)	C1—N1—Cu1	144.2 (2)
N10—Cu1—N40	97.52 (9)	N1—C1—N3	173.5 (3)
N1—Cu1—N40	136.63 (10)	C1—N3—C2	119.2 (3)
N30—Cu1—N20	97.32 (9)	N2—C2—N3	174.2 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12 \cdots F1 ⁱⁱⁱ	0.95	2.28	3.154 (4)	153
C22—H22 \cdots F3 ^{iv}	0.95	2.43	3.107 (3)	128
C32—H32 \cdots F2	0.95	2.59	3.484 (3)	158
C33—H33 \cdots F4	0.95	2.49	3.261 (3)	138
C33—H33 \cdots F4 ⁱⁱ	0.95	2.53	3.173 (3)	125
C34—H34 \cdots F1 ⁱⁱ	0.95	2.35	3.292 (3)	171
C43—H43 \cdots F3 ^v	0.95	2.53	3.274 (3)	135
C46—H46 \cdots F3 ⁱ	0.95	2.35	3.198 (3)	148

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

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