Bis(2,2'-bipyridine)(dicyanamido)-copper(II) tetrafluoroborate

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In the title compound, $[Cu(C_2N_3)(C_{10}H_8N_2)_2]BF_4$, the Cu^{II} atom shows distorted trigonal-bipyramidal geometry, with the dicyanamido ligand in the equatorial plane. The two out-of-plane Cu—N bond lengths to bipyridine are 2.006 (3) and 1.998 (3) Å, whereas the in-plane Cu—N distances are 2.142 (3) and 2.043 (3) Å to the bipyridine, and 2.015 (3) Å to the dicyanamide.

Comment

Understanding the shape of coordination polyhedra (SCP) in the case of five-coordination is one of the current problems in coordination chemistry. Although electrostatic calculations for ML_5 compounds show that a trigonal bipyramid (TBP), with larger axial than equatorial bond lengths, is energetically slightly preferred over a square pyramid (SP), with equatorial bonds longer than apical bonds (Kepert, 1982), the usual SCP in the case of Cu^{II} compounds is trigonal bipyramidal with some degree of distortion towards SP. This contradiction with electrostatic calculations could be caused by either steric effects of the ligands or electronic effects at the Cu^{II} atom (Jahn–Teller effect). A number of different structural approaches have been used in the past to describe the geometries of five-coordinated compounds (Addison *et al.*, 1984; Potočňák *et al.*, 1997; Baran, 1990; Holmes & Deiters, 1977; Muetterties & Guggenberger, 1974). Among these, Harrison & Hathaway (1980) proposed the use of three equatorial angles as a criterion to classify $[Cu(bpy)_2X]Y$ compounds into three groups with respect to the distortion of the Cu polyhedron: compounds with angles $\alpha_1 - \alpha_2 < 15°$ (for a more exact definition of the α angles, see below) and $\alpha_3 = 95–130°$ are best considered as trigonal bipyramidal with near C_{2v} symmetry; compounds with $\alpha_1 - \alpha_2 > 20°$ and $\alpha_3 < 120°$ are distorted trigonal bipyramidal with square-pyramidal distortion; and compounds with $\alpha_1 - \alpha_2 > 20°$ and $\alpha_3 > 120°$ are intermediate in stereochemistry between trigonal bipyramidal

and square pyramidal. Recent papers by Hathaway's group (Murphy, Nagle *et al.*, 1997; Murphy, Murphy *et al.*, 1997; Murphy *et al.*, 1998; O'Sullivan *et al.*, 1999) show eight different modes of distortion of TBP, but it is rather difficult to describe quantitatively the degree of distortion of the TBP polyhedron towards SP using these modes and the above-mentioned criteria.

With the aim of finding out 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 $[CuL_2X]Y$, where L is 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy), X is an N-donor pseudohalide anion and Y is the tricyanomethanide anion, $[C(CN)_3]^-$ (Potočňák *et al.*, 2001). The SCP in those compounds with the same counter-anion is more or less distorted trigonal bipyramidal. To describe the distortion of TBP towards SP we have used the above-mentioned criteria and compared them with possible electronic criteria (Hathaway, 1972). 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 $[Cu(bpy)_2N(CN)_2]X$, where X is an anion of charge 1−. The structure of the first compound in this series, with $X = [C(CN)_3]^-$, has already been published (Potočňák *et al.*, 2001). Here, we present the structure of the title compound, $[Cu(bpy)_2N(CN)_2]BF_4$, (I).
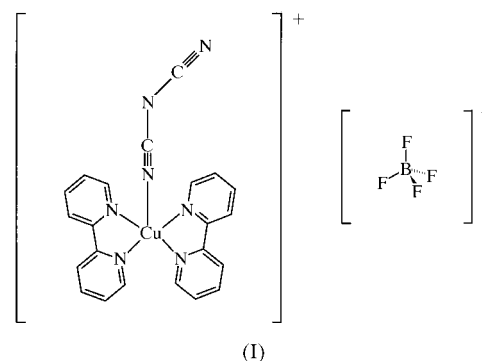

(I)

Fig. 1 shows the labelling scheme of one formula unit of (I). The Cu atom is fivefold coordinated by two bpy molecules and one $N(CN)_2^-$ ligand (in the equatorial plane). The coordination polyhedron is a distorted trigonal bipyramid. The BF_4^- anion does not enter the inner coordination sphere. In the trigonal bipyramid, the two out-of-plane Cu—N1 and Cu—N3 distances are nearly equal [2.006 (3) and 1.998 (3) Å, respectively], and are almost collinear [N1—Cu—N3 = 177.52 (12)°]. The two in-plane distances (Cu—N2 and Cu—N4) of 2.142 (3) and 2.043 (3) Å, respectively, are longer than the out-of-plane Cu—N distances by an average of 0.091 Å, which is a feature generally observed for compounds with $[Cu(L)_2X]$ cations, 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 *et al.*, 2001). The third in-plane Cu—N5 [N from the $N(CN)_2$ ligand] distance of 2.015 (3) Å is shorter

than the other two in-plane distances but is longer than the out-of-plane distances. This differs from the situation found in [Cu(bpy)₂N(CN)₂][C(CN)₃], (II) (Potočňák *et al.*, 2001), where this is the shortest Cu—N bond, and in the related compound [Cu(phen)₂N(CN)₂][C(CN)₃], (III), where this bond is of the same length (within 1σ) as the two out-of-plane bonds (Potočňák *et al.*, 1996).

The out-of-plane angles lie within the range 79.11 (11)– 97.17 (12)°, similar to those observed in (II) and (III). In the following discussion, the values in square brackets are those observed in (II) and (III), respectively. The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one large angle of 145.00 (13)° (α_1 = N5—Cu—N4) [140.0 (2) and 133.6 (2)°], and two small angles of 108.55 (12)° (α_2 = N5—Cu—N2) [112.4 (2) and 115.7 (2)°] and 106.44 (11)° (α_3 = N2—Cu—N4) [107.6 (2) and 110.70 (13)°]. Thus, the α_3 angle, which is opposite to the Cu— N5 bond, is narrower than the ideal angle of 120° by 13.56°, and there is a difference of 36.45° between α_1 and α_2. Therefore, according to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom in (I) can be best described as distorted trigonal bipyramidal with square-pyramidal distortion, similar to (II), with atom N2 in the apical position of the square pyramid. In contrast, according to the values of the α_1, α_2 and α_3 angles for (III), its coordination polyhedron can be best described as trigonal bipyramidal with near C_{2v} symmetry. The difference in the SCP is in accordance with the values of the τ parameter, which is 54.2 for (I), 58.5 for (II) and 69.2 for (III) [$\tau = (\Theta - \Phi)/0.6$, where Θ (N3—Cu—N1) and Φ (N5—Cu—N4) are the two largest angles around the central atom; hence, the τ parameter is 100 or 0 for an ideal trigonal bipyramid or square pyramid, respectively; Addison *et al.*, 1984]. This difference in the SCP of (I) and (II) on one hand, and of (III) on the other, could be explained by the reduced rigidity of the bpy ligand in comparison with the phen molecule. Whereas the phen molecule is essentially planar, the two pyridine rings in a bpy molecule can rotate around the single C—C bond. The inter-

planar angles are 3.2 (1)° for the first bpy molecule (N1–N2) and 8.0 (1)° for the second (N3–N4) [9.1 (2) and 4.2 (3)°, respectively, for (II)]. The sum of the bond angles in the equatorial plane of (I) (359.99°) indicates coplanarity of the Cu atom with the three equatorial atoms [the deviation of the Cu atom from the N2/N3/N5 plane is 0.009 (1) Å towards N1].

There are three canonical formulae describing the mode of bonding in a dicyanamido ligand. Inspection of the bond lengths (Table 1) shows that no canonical formula properly describes the bonding mode in this particular dicyanamide. Both the N_{cyano}≡C [N5≡C5 1.135 (5) and N6≡C6 1.146 (5) Å] and N_{amide}=C distances [N7=C5 1.291 (5) and N7=C6 1.322 (5) Å] are usual for N≡C triple (1.15 Å) and N=C double bonds (1.27 Å), respectively. The N7—C5—N5 and N7—C6—N6 angles [173.7 (4) and 174.3 (4)°, respectively] are almost linear, while the value of the C5—N7—C6 angle is 119.6 (3)°. The dicyanamido ligand is planar, the largest deviation of atoms from the mean plane being 0.007 (4) Å. According to Golub *et al.* (1986), the bonding mode of dicyanamide to the Cu atom can be considered as angular [C5—N5—Cu 141.7 (3)°].

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* ethanolic solution of bpy (10 ml). To the resulting blue solution, a 0.1 *M* aqueous/ethanolic solution of KN-(CN)₂ (6 ml) was added (all solutions were warmed before mixing). Blue crystals of the title complex appeared by the next day.

Crystal data

[Cu(C₂N₃)(C₁₀H₈N₂)₂]BF₄	Mo $K\alpha$ radiation
M_r = 528.77	Cell parameters from 8000
Orthorhombic, *Pbca*	reflections
a = 8.6469 (5) Å	θ = 10.6–29.5°
b = 17.8651 (8) Å	μ = 1.044 mm⁻¹
c = 28.7434 (15) Å	T = 193 (2) K
V = 4440.2 (4) Å³	Prism, blue
Z = 8	0.35 × 0.24 × 0.11 mm
D_x = 1.582 Mg m⁻³	

Data collection

Stoe IPDS diffractometer	θ_{max} = 27.50°
φ scans	$h = -11 \rightarrow 11$
28 872 measured reflections	$k = -23 \rightarrow 17$
5090 independent reflections	$l = -37 \rightarrow 37$
2958 reflections with $I > 2\sigma(I)$	Intensity decay: none
R_{int} = 0.065	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + (0.0938P)^2]$
$wR(F^2)$ = 0.141	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.865	$(\Delta/\sigma)_{max} < 0.001$
5090 reflections	$\Delta\rho_{max}$ = 0.55 e Å⁻³
316 parameters	$\Delta\rho_{min}$ = −0.56 e Å⁻³
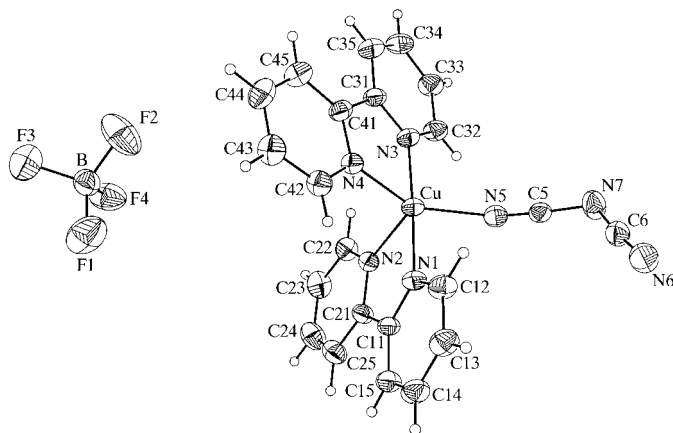
Figure 1
ORTEP (Siemens, 1994) drawing of the formula unit of (I) with the atom-labelling scheme. Displacement ellipsoids are plotted at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

All H atoms were located from a difference Fourier map and were refined using a riding model (C—H = 0.93 Å), with isotropic displacement parameters 1.2 times those of their parent C atoms. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*97 (Sheldrick, 1997).

Table 1
Selected geometric parameters (Å, °).

Cu—N3	1.998 (3)	C5—N5	1.135 (5)
Cu—N1	2.006 (3)	C5—N7	1.291 (5)
Cu—N5	2.015 (3)	C6—N6	1.146 (5)
Cu—N4	2.043 (3)	C6—N7	1.322 (5)
Cu—N2	2.142 (3)		
N3—Cu—N1	177.52 (12)	N1—Cu—N2	79.11 (11)
N3—Cu—N5	92.35 (12)	N5—Cu—N2	108.55 (12)
N1—Cu—N5	90.03 (12)	N4—Cu—N2	106.44 (11)
N3—Cu—N4	80.48 (12)	N5—C5—N7	173.7 (4)
N1—Cu—N4	97.17 (12)	C5—N5—Cu	141.7 (3)
N5—Cu—N4	145.00 (13)	N6—C6—N7	174.3 (4)
N3—Cu—N2	100.75 (12)	C5—N7—C6	119.6 (3)

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97; molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1434). Services for accessing these data are described at the back of the journal.

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