Chlorobis(1,10-phenanthroline-$\kappa^2 N,N'$)copper(II) dicyanamide

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In the complex cation of the title compound, [CuCl-(C₁₂H₈N₂)₂][N(CN)₂], the Cu atom is five-coordinated, within a distorted trigonal bipyramid, by two 1,10-phenanthroline molecules and one Cl ligand. The Cl ligand is coordinated in the equatorial plane and lies, along with the Cu atom, on the twofold rotation axis. The axial Cu—N distances are substantially shorter than the equatorial Cu—N distances. A twofold rotation axis passes through the central N atom of the anion.

Comment

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 establishing the possible reasons for different SCP in related compounds, we have previously studied the structures of five-coordinate copper(II) complexes of the general formula [Cu(*L*-*L*)₂(dca)]*Y*, where *L*-*L* is 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy), dca is dicyanamide and *Y* is [CF₃SO₃]⁻, [ClO₄]⁻, [PF₆]⁻, [C(CN)₃]⁻ or [BF₄]⁻ (Potočňák *et al.*, 2005). We have observed that the SCP in compounds with *L*-*L* = bpy is slightly more distorted trigonal–bipyramidal than that in compounds containing phen. In order to verify this finding, we have attempted to prepare compounds with *Y* = Cl and have checked their SCP. As a result of our attempts, the title compound, [Cu(phen)₂Cl]dca, (I), with coordinated Cl and uncoordinated dca anions, has been prepared and we present its structure here.

(I)
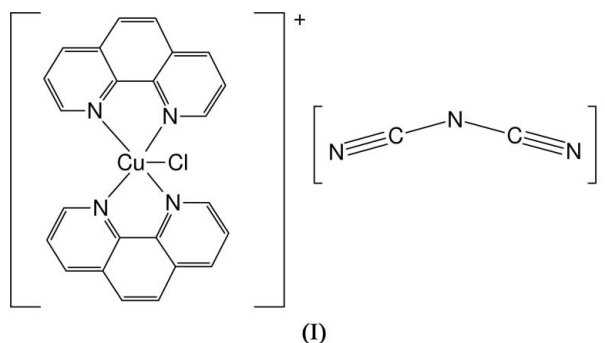
Compound (I) is composed of discrete [Cu(phen)₂Cl]⁺ complex cations and uncoordinated [N(CN)₂]⁻ anions (Fig. 1). Atom Cu1, on a twofold rotation axis, is five-coordinated by two phen molecules and one Cl⁻ anion. The Cl ligand is coordinated in the equatorial plane and lies on the same rotation axis. The coordination polyhedron is a distorted trigonal bipyramid. The dca anion, which has a twofold rota-
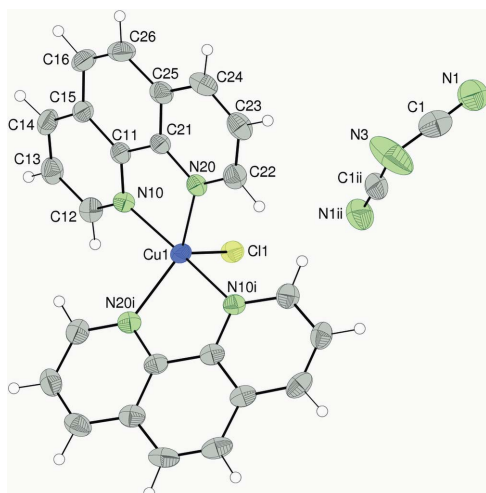
Figure 1
The ions of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 85% probability level [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$, (ii) $1 - x, y, \frac{3}{2} - z$].
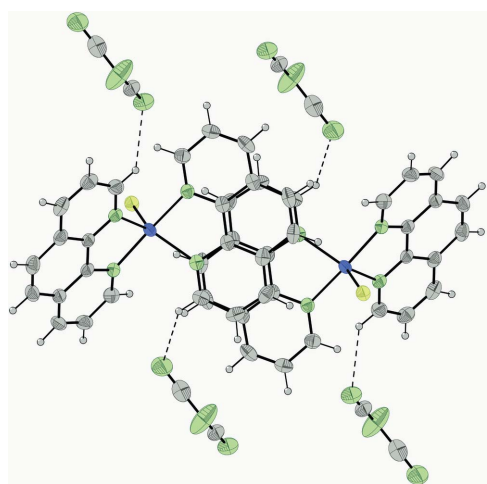

Figure 2
Intermolecular C—H$\cdots$N hydrogen bonds (dashed lines) and possible π–π interactions between parallel phen ligands at $(\frac{3}{2} - x, \frac{3}{2} - y, 1 - z)$.

tion axis passing through N3, does not enter the inner coordination sphere. In the trigonal bipyramid, the two axial Cu1—N10 [1.9956 (18) Å] bonds are almost collinear and are shorter by 0.106 Å than the two equatorial Cu1—N20 [2.1018 (13) Å] bonds (Table 1), which is a feature generally observed for compounds with the [Cu(L-L)$_2$Cl]$^+$ cation, where L-L = bpy (O'Sullivan et al., 1999; Jia et al., 2005) or phen (Murphy et al., 1998; Lu et al., 2004).

The bond angles (Table 1) in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one wide N20—Cu1—N20^i angle [133.44 (5)°], and two narrow Cl1—Cu1—N20 and Cl1—Cu1—N20^i angles [113.28 (4)°] [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. Given these values, the coordination polyhedron around atom Cu1 can be best described as trigonal–bipyramidal with approximate C_{2v} symmetry (Harrison & Hathaway, 1980). This is in accordance

with the value of $\tau = 0.696$ [$\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid (Addison et al., 1984)].

The crystal structure of (I) is stabilized by intermolecular C—H$\cdots$N hydrogen bonds (Table 2) and possible π–π interactions between the parallel phen ligands at (x, y, z) and $(\frac{3}{2} - x, \frac{3}{2} - y, 1 - z)$, with a distance between the mean planes of 3.433 Å.

Experimental

Crystals of (I) were prepared by mixing a 0.1 M aqueous solution of CuCl$_2$ (5 ml) with a 0.1 M ethanolic 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). A mixture of green crystals of (I) and dark green crystals of [Cu(phen)(dca)$_2$] appeared after 2 d. The crystals were filtered off, dried in air and separated under a microscope.

Crystal data

[CuCl(C$_{12}$H$_8$N$_2$)$_2$](C$_2$N$_3$)	$Z = 4$
$M_r = 525.5$	$D_x = 1.634$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.9595$ (8) Å	$\mu = 1.18$ mm^{-1}
$b = 10.6537$ (5) Å	$T = 120$ K
$c = 14.7190$ (8) Å	Needle, green
$\beta = 114.481$ (5)°	$0.60 \times 0.15 \times 0.13$ mm
$V = 2134.9$ (2) Å^3	

Data collection

Oxford Diffraction XCalibur-2 ddiffractometer with area-detector Sapphire-2	Diffraction, 2004)
	$T_{min} = 0.745$, $T_{max} = 0.863$
ω scans	18086 measured reflections
	2179 independent reflections
Absorption correction: numerical (CrysAlis RED; Oxford	1844 reflections with $I > 3\sigma(I)$
	$R_{int} = 0.025$
	$\theta_{max} = 26.4°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(I) + 0.0016I^2]$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.007$
$S = 1.25$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
2179 reflections	$\Delta\rho_{min} = -0.15$ e Å^{-3}
160 parameters	

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.3876 (6)	N1—C1	1.150 (3)
Cu1—N10	1.9956 (18)	N3—C1	1.321 (2)
Cu1—N20	2.1018 (13)		
Cl1—Cu1—N10	92.39 (4)	N10—Cu1—N20^i	96.67 (6)
Cl1—Cu1—N20	113.28 (4)	N20—Cu1—N20^i	133.44 (5)
N10—Cu1—N10^i	175.22 (6)	C1—N3—C1^{ii}	118.9 (2)
N10—Cu1—N20	81.42 (6)	N3—C1—N1	174.8 (2)

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
C22—H22$\cdots$N1^{ii}	0.96	2.56	3.307 (3)	135

Symmetry code: (ii) $-x + 1, y, -z + \frac{3}{2}$.

H atoms were positioned geometrically, with C—H = 0.96 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000* (Petříček & Dušek, 2000); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *JANA2000*.

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