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Bis(4,5-diazafluoren-9-one)dicyanamidocopper(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.102
Data-to-parameter ratio = 11.7

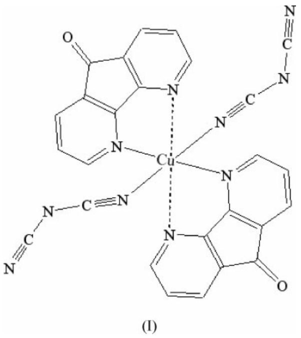
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Bright-blue crystals of the centrosymmetric title compound, $[Cu(C_2N_3)_2(C_{11}H_6N_2O)_2]$, were obtained by reacting copper(II) chloride with 4,5-diazafluoren-9-one (dafo) and sodium dicyanamide. X-ray diffraction analysis reveals that the dicyanamide and dafo ligands are bonded to the Cu atom to give a distorted octahedral geometry. The dicyanamide anions are terminally bonded in *trans* postitions. Weak C—H···O and C—H···N interactions help to define the crystal packing.

Comment

4,5-Diazafluoren-9-one, $C_{11}H_6N_2O$ (dafo), which has an exocyclic keto function, is currently attracting research attention, perhaps because of its DNA intercalation properties (Pyle *et al.*, 1989; Kulkarni *et al.*, 2001, 2002). The reactive exocyclic keto function in dafo offers distinct advantages for further derivatization, to yield multinuclear metal complexes having interesting catalytic and biological properties. Studies of the neutral dafo ligand are still limited (Lu *et al.*, 1996; Balagopalakrishna & Rajasekharan, 1992; Wang *et al.*, 1995). It has been well documented that the large N—N bite distance (2.99 Å) enforced by the rigid five-membered central ring leads to unequal binding by the two N atoms with smaller metal atom ions, such as Cu^{II}.

Polymeric complexes comprising transition metals with dicyanamide have attracted considerable attention because of their interesting coordination (Wang *et al.*, 2000; Batten *et al.*, 1999; Balagopalakrishna & Rajasekharan, 1992). By introducing different co-ligands, such as pyridine, bipyridine *etc.*, various types of structure have been obtained. We have been interested in constructing dicyanamide-bridged Cu^{II} coordination polymers. Using dafo, dicyanamide and Cu^{2+} in a molar ratio of 1:2:1, we unexpectedly obtained the title novel mononuclear Cu^{II} complex, $Cu(dafo)_2[N(CN)_2]_2$, (I) (Fig. 1), which has both neutral and anionic ligands in the molecule. In this communication, we describe the synthesis and crystal structure of (I).



(I)

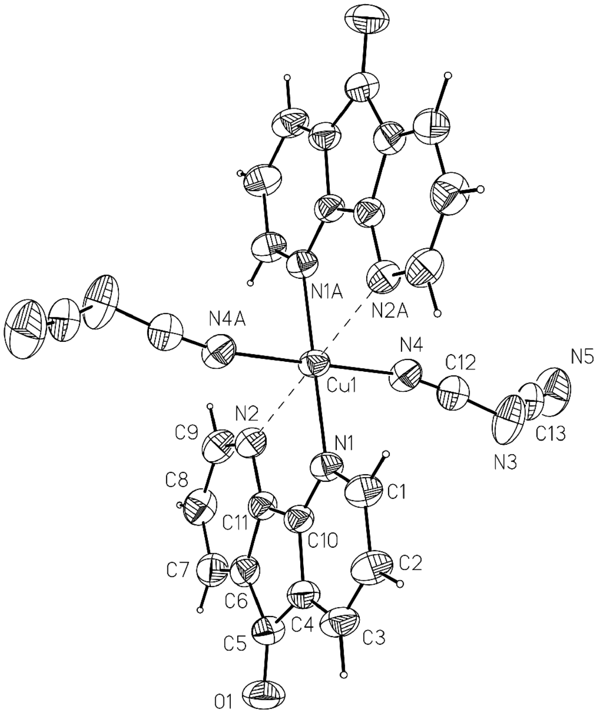


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (A) $2 - x, -y, -z$.]

The coordination environment of the Cu^{II} ion in (I) can be described as elongated octahedral; it sits on a centre of symmetry. The two N donor atoms of dafo and the two N atoms of two $N(CN)_2^-$ anions constitute the equatorial plane, while the remaining two N atoms of dafo occupy the axial positions. The equatorial $Cu-N_{dafo}$ distance is 1.954 (3) Å, which is similar to that in $[Cu(C_2N_3)_2(phen)]_n$ (phen is 1,10-phenanthroline; Wang *et al.*, 2000) and $[Cu(dafo)_2(H_2O)_2](ClO_4)_2$ (Zhang *et al.*, 2003), while the equatorial $Cu-N_{dicyanamide}$ bond length is 2.001 (3) Å. The equivalent axial Cu—N bond distances are 2.684 (3) Å. A similar coordination mode for dafo has been observed in other Cu–dafo complexes (Zhang *et al.*, 2003). This difference is presumed to result from the long N1···N2 distance.

The dicyanamide ligand possesses pseudo-C_{2v} symmetry, with C≡N bond distances of 1.109 (5) and 1.118 (5) Å. The C—N—C angle of 124.0 (4)°, and N—C—N angles of 171.7 (5) and 172.2 (5)°, are comparable with the values found in other dicyanamide complexes (Batten *et al.*, 1998; Shi *et al.*, 1995; Escure *et al.*, 2000; Yeung *et al.*, 2003; Carranza *et al.*, 2002; Sun *et al.*, 2000; Kožíšek *et al.*, 1996; Marshall *et al.*, 2000).

As shown in Fig. 2 and Table 2, two kinds of weak intermolecular hydrogen bonds exist in the structure of (I), involving C—H···O or C—H···N interactions. The former type involves a bond from C3—H3*A* to the dafo atom $O1^{iii}$ (symmetry code as in Table 2), which connects adjacent molecules to give rise to a quasi-one-dimensional chain, as shown in Fig. 2. These chains are further linked, through C1—H1*A*···$N5^{i}$ and C9—H9*A*···$N5^{ii}$ interactions (Table 2; symmetry codes as in Table 2), generating an extended network.

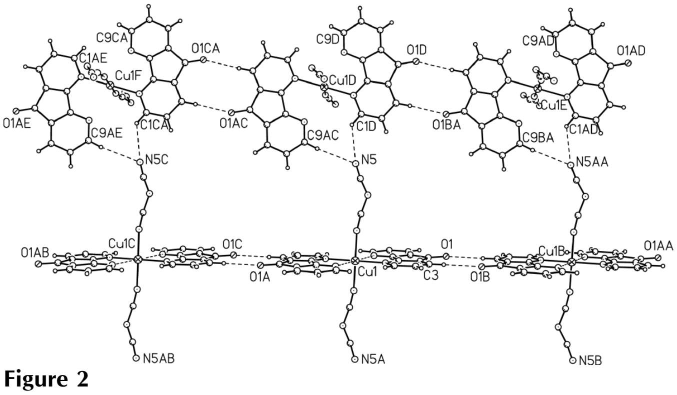


Figure 2
Detail of the packing of (I), showing the weak intermolecular interactions [symmetry codes: (A) $2 - x, -y, -z$; (B) $1 - x, -y, 1 - z$; (AA) $x - 1, y, z + 1$; (C) $1 + x, y, z - 1$; (AB) $3 - x, -y, -z - 1$; (D) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (AC) $3 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (AD) $x, \frac{1}{2} - y, \frac{3}{2} + z$; (E) $x, \frac{1}{2} - y, \frac{3}{2} + z$; (BA) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (F) $2 - x, y - \frac{1}{2}, -z - \frac{3}{2}$; (CA) $2 - x, y - \frac{1}{2}, -z - \frac{3}{2}$; (AE) $x, -\frac{1}{2} - y, z - \frac{3}{2}$].

The present work has thus revealed that, for dafo–copper(II) complexes, the bite distance of the donor N atoms dictates the overall geometry of the resulting metal complexes. This is due to the rigid five-membered ring of dafo, which enlarges the N···N bite distance compared with the analogous 2,2′-bipyridine. Consequently, the long N···N distance of dafo has an unfavourable effect on the formation of a five-membered chelating ring with transition metal ions.

In many cases, dicyanamide can serve as a bridging ligand, and so we introduced it in order to prepare a bridged complex. However, the resulting mononuclear complex, (I), was unexpected. This result reveals that the sterically hindered effect of dafo dominates the formation of a mononuclear molecule.

Experimental

4,5-Diazafluorenone (dafo) was prepared by the procedure reported by Henderson *et al.* (1984). A solution of $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol) with dafo (17.6 mg, 0.1 mmol) in methanol–H_2O (1:1 *v*/*v*, 10 ml) was layered on to an aqueous solution of $NaN(CN)_2$ (5 ml, 0.2 mmol, 17.8 mg). Blue single crystals of (I) were obtained over a period of one week (yield 30%).

Crystal data

$[Cu(C_2N_3)_2(C_{11}H_6N_2O)_2]$
$M_r = 560.00$
Monoclinic, $P2_1/c$
$a = 8.2935$ (12) Å
$b = 14.9729$ (10) Å
$c = 9.7568$ (11) Å
$\beta = 101.192$ (11)°
$V = 1188.5$ (2) $Å^3$
$Z = 2$
$D_x = 1.565$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.9–11.4°$
$\mu = 0.97$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.25 × 0.15 × 0.10 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.855$, $T_{max} = 0.908$
2758 measured reflections
2090 independent reflections
1524 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 17$
$l = -11 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.10$
2090 reflections
178 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 1.2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	1.954 (3)	N3—C13	1.307 (6)
Cu1—N1	2.001 (3)	N4—C12	1.118 (5)
Cu1—N2	2.684 (3)	N5—C13	1.109 (5)
N3—C12	1.301 (5)		
N2—Cu1—N1	77.7 (3)	C1—N1—Cu1	127.9 (2)
N4—Cu1—N2	89.8 (4)	C12—N3—C13	124.0 (4)
N4—Cu1—N1	88.74 (12)	C12—N4—Cu1	168.6 (3)
C10—N1—C1	115.8 (3)	N4—C12—N3	171.7 (5)
C10—N1—Cu1	116.2 (2)	N5—C13—N3	172.2 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···N5^{i}	0.93	2.54	3.260 (3)	134
C9—H9A···N5^{ii}	0.93	2.69	3.605 (3)	170
C3—H3A···O1^{iii}	0.93	2.42	3.352 (3)	177

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

All H atoms bound to C atoms, which were visible in difference maps, were placed in idealized positions and refined as riding, with C—H distances of 0.93 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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