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One-dimensional chain structure of *catena*-poly[[[(1,10-phenanthroline)copper(II)]-μ-dicyanamido] perchlorate]

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The crystal structure of the title compound, $[Cu(C_{12}H_8N_2)\{N(CN)_2\}](ClO_4)$, consists of zigzag chain $[Cu(phen)(dca)]_n^{n+}$ cations and $[ClO_4]^-$ anions (phen = 1,10-phenanthroline and dca = $[N(CN)_2]^-$). The Cu^{II} atom has a near square planar coordination environment with two N atoms of phen ligands and two N-terminal atoms of dca ligands. The complex forms a one-dimensional chain structure along the *c* axis, using dca as an end-to-end bridging ligand. The hydrogen-bonding interactions produce a three-dimensional network.

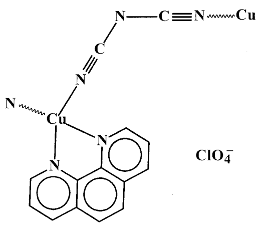
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.115
Data-to-parameter ratio = 13.1

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

Comment

In recent years, metal–dicyanamide (dca, $[N(CN)_2]^-$) coordination chemistry has become a fast growing research field because of its interesting coordination and physical properties (Marshall *et al.*, 2002; Shi *et al.*, 2002; Brown & Manson, 2002). Since dicyanamide has three N-donor atoms, it can exhibit several possible coordination modes (Marshall *et al.*, 2002; Shi *et al.*, 2002). Complexes formulated as $[M(dca)_2]_n$ (M = Mn, Fe, Co, Ni, Cu, Zn, Ag, *etc.*) containing only dca have been synthesized; these are of a quite limited structural type (Batten *et al.*, 1998, 1999; Jensen, Batten, Fallon, Moubaraki *et al.*, 1999; Jensen *et al.*, 2000; Kurmoo & Kepert, 1998; Manson, Lee *et al.*, 1998; Britton, 1990). By introducing co-ligands that may be monodentate or bidentate ligands, such as pyridine, bipyridine, 1,10-phenanthroline, 2,2′-biimidazole *etc.*, many complexes have been synthesized with various interesting structures (Manson, Incarvito *et al.*, 1998; Manson *et al.*, 1999; Jensen, Batten, Fallon, Hockless *et al.*, 1999; Batten *et al.*, 1999; Wang, Luo, Sun, Yan, Gao & Liao, 2000; Wang, Luo, Sun, Yan, Liao & Gao, 2000; Sun *et al.*, 2000; Werff *et al.* 2001). As an extension of this research area, we have synthesized a new one-dimensional complex $[Cu(1,10\text{-}phen)(dca)](ClO_4)$, (I). Here we report the preparation and crystal structure of (I).



(I)

The coordination of the Cu atom in (I) is similar to that in the complex [Cu(dca)(MeCN)] reported by Batten *et al.* (2000). The Cu^{II} atom is coordinated by two terminal N atoms of two different $[N(CN)_2]^-$ ligands [Cu1—N3 1.978 (2) Å and

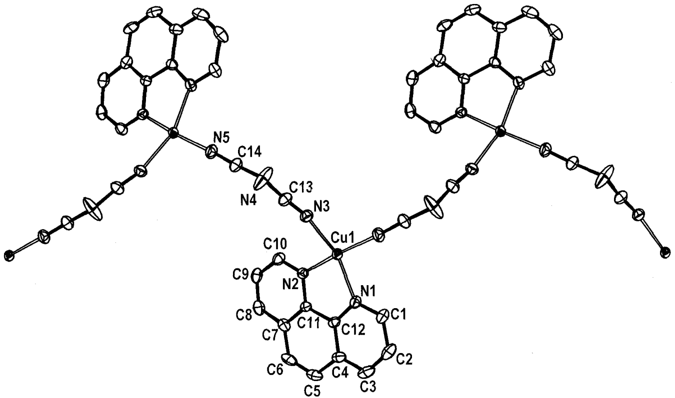


Figure 1
The cationic chain structure of the title complex, with displacement ellipsoids at the 30% probability level.

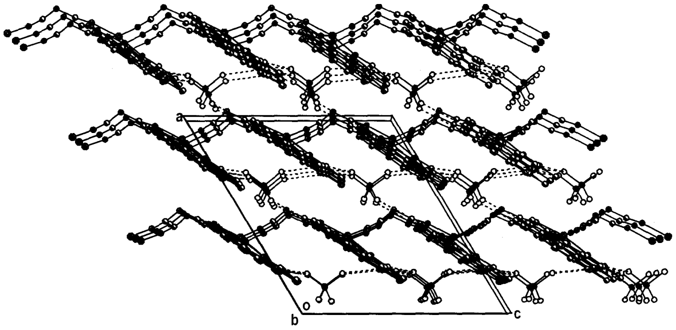


Figure 2
The three-dimensional framework of the complex formed through hydrogen-bond interactions. The hydrogen bonds are represented by dotted lines.

Cu1—N5^{i} 1.948 (2) Å; symmetry code: (i) x, $-y$, $z-\frac{1}{2}$] and two N atoms of phen ligands [Cu1—N1 2.017 (2) Å and Cu1—N1 1.996 (2) Å]. The Cu and four coordinating N atoms (N1, N2, N3 and N5) constitute a near square-planar geometry and deviate from the mean plane by 0.087, −0.323, 0.286, −0.302 and 0.253 Å, respectively. The Cu—N distances are in good agreement with those found in the complexes reported by Wang, Luo, Sun, Yan, Gao & Liao (2000) and Potočňák *et al.* (1996). Each $[N(CN)_2]^-$ is coordinated to two metal atoms *via* the two nitrile N atoms. The $[N(CN)_2]^-$ ligands bridge end-to-end the Cu^{II} atoms into a one-dimensional zigzag chain extended along the *c* axis, as shown in Fig. 1; between these chains the $[ClO_4]^-$ anions are located, as shown in Fig. 2. The parallel chains are further connected by C—H···O hydrogen bonds, involving three O atoms of the $[ClO_4]^-$ anion and C atoms of phen (Table 2). It is worth noting that the $[ClO_4]^-$ anion is ordered due to the hydrogen-bond interactions.

Experimental

An aqueous solution of $Cu(ClO_4)_2$ (1*M*, 0.5 ml) and 4 ml of an aqueous solution of Na(dca) (1 mmol, 91 mg) were thoroughly mixed, then 10 ml of an ethanol solution of 1,10-phen (0.5 mmol, 99 mg) was added dropwise with stirring. The resulting mixture was filtered and the filtrate was left undisturbed at room temperature. Transparent green, needle-like crystals were obtained after a few days.

Crystal data

$[Cu(C_2N_3)(C_{12}H_8N_2)](ClO_4)$
$M_r = 409.24$
Monoclinic, *Cc*
$a = 14.260$ (5) Å
$b = 9.660$ (2) Å
$c = 12.789$ (5) Å
$\beta = 120.878$ (12)°
$V = 1512.0$ (9) Å^3
$Z = 4$
$D_x = 1.798$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2248 reflections
$\theta = 3.3$–27.5°
$\mu = 1.65$ mm^{-1}
$T = 293$ (2) K
Needle, green
0.50 × 0.15 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
$T_{min} = 0.774$, $T_{max} = 1.000$
5925 measured reflections
2952 independent reflections
2571 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.115$
$S = 1.05$
2952 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.0356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), 1704 Friedel pairs
Flack parameter = 0.03 (2)

Table 1
Selected geometric parameters (Å, °).

Cu1—N5^{i}	1.9482 (19)	N5—Cu1^{ii}	1.9482 (19)
Cu1—N3	1.9778 (16)	N4—C14	1.307 (3)
Cu1—N2	1.9956 (17)	N4—C13	1.308 (3)
Cu1—N1	2.0170 (16)	N3—C13	1.124 (2)
N5—C14	1.132 (3)		
N5^{i}—Cu1—N3	94.43 (8)	O2—Cl1—O1	110.40 (13)
N5^{i}—Cu1—N2	168.11 (5)	O3—Cl1—O1	108.27 (11)
N3—Cu1—N2	92.88 (7)	C14—N5—Cu1^{ii}	169.85 (14)
N5^{i}—Cu1—N1	94.37 (7)	C14—N4—C13	123.37 (19)
N3—Cu1—N1	155.92 (5)	C13—N3—Cu1	165.54 (14)
N2—Cu1—N1	82.60 (7)	C1—N1—Cu1	129.50 (14)
O4—Cl1—O2	109.14 (12)	C12—N1—Cu1	111.90 (13)
O4—Cl1—O3	108.92 (11)	C10—N2—Cu1	129.69 (13)
O2—Cl1—O3	111.04 (13)	C11—N2—Cu1	112.34 (13)
O4—Cl1—O1	109.02 (13)	N5—C14—N4	171.13 (19)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···O1^{iii}	0.93	2.56	3.301 (4)	138
C6—H6*A*···O2^{iv}	0.93	2.56	3.368 (3)	146
C10—H10*A*···O2^{v}	0.93	2.39	3.193 (3)	145
C10—H10*A*···O4^{vi}	0.93	2.91	3.261 (3)	104

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

H atoms were positioned geometrically, assigned isotropic displacement parameters, and allowed to ride on their respective parent C atoms.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*97 (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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