

catena-Poly[[dicyanamido(1,10-phenanthroline)copper(II)]- μ -dicyanamido]

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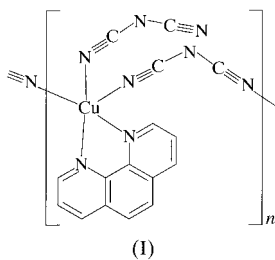
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The title compound, $[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)]_n$, has a sheet-like structure, built by $[\text{Cu}(\text{phen})(\text{dca})_2]_n$ (phen is 1,10-phenanthroline and dca is dicyanamide) chains which are interconnected by secondary long Cu–N bonds between the chains. The Cu^{2+} ion is in a distorted tetragonal bipyramidal (5 + 1) coordination environment. The sheets stack into the three-dimensional crystal structure through aromatic interactions between the coordinated phen ligands of adjacent sheets.

Comment

Polymeric complexes comprised of transition metals with dicyanamide have attracted considerable attention because of their interesting coordination and physical properties (Kurmo & Kepert, 1998; Manson, Kmety *et al.*, 1998; Manson, Arif & Miller, 1999; Batten *et al.*, 1999; Jensen *et al.*, 1999; van Albada *et al.*, 2000). Those complexes containing only dca are of a quite limited structural type (Kurmo & Kepert, 1998; Manson, Kmety *et al.*, 1998; Jensen *et al.*, 1999), while by introducing co-ligands such as pyridine, bipyridine *etc.*, various types of structure have been obtained, and this presents an opportunity to adjust the physical properties (Manson, Incarvito *et al.*, 1998; Manson, Arif & Miller, 1999; Manson, Arif, Incarvito *et al.*, 1999; Batten *et al.*, 1999). So far, only a few such Cu complexes have been structurally characterized



(van Albada *et al.*, 2000). Recently, we have synthesized the title compound, (I), which has an extended structure, and its crystal structure is reported here.

Basically, the structure is sheet-like, consisting of inter-linked $[\text{Cu}(\text{phen})(\text{dca})_2]_n$ chains. In the chain, each Cu^{2+} ion is fivefold coordinated by the N atoms of three dca ligands and one phen ligand (Fig. 1). The CuN_5 moiety can be described as a distorted square pyramid, because the trigonality criterion, which is 1 for an ideal trigonal bipyramid and 0 for an ideal square pyramid (Addison *et al.*, 1984), is 0.13 for the moiety. The two terminal N atoms from two dca ligands and the two N atoms of the phen ligand form the base of the pyramid. The Cu^{2+} ion is 0.183 (1) Å above the base. The apical position is

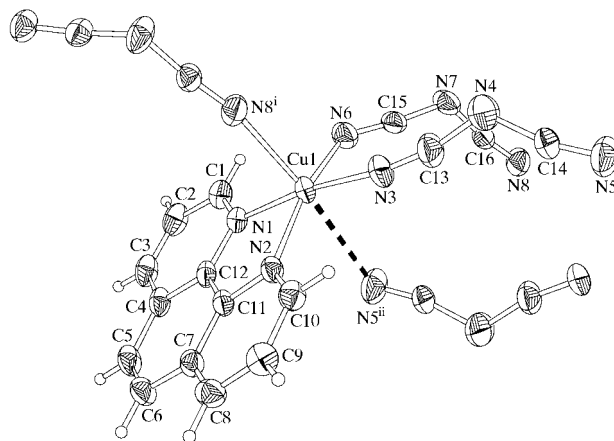


Figure 1

The local coordination environment of the Cu^{2+} ion with the atom-numbering scheme and 30% probability displacement ellipsoids. The symmetry codes are as in Table 1. The dashed bond shows the secondary long Cu–N bond.

occupied by the terminal N atom of a neighbouring dca ligand. Thus, adjacent CuN_5 pyramids are linked by a bridging dca ligand from the apex of one pyramid to the base of the next one to form a zigzag chain running along the *c* direction (Fig. 2). Since the adjacent Cu centres are related to each other by the *c*-glide plane, all phen ligands attached to the same chain are on the same side of the chain. The plane of the phen ligand and that of the base of the pyramid are approximately coplanar. Of the three dca ligands coordinated to each Cu atom, two are bridging ligands connecting Cu centres and the third is terminal. In fact, these terminal dca ligands cross-link adjacent $[\text{Cu}(\text{phen})(\text{dca})_2]_n$ chains through secondary long Cu–N bonds involving the terminal N atoms to give a sheet-like structure which extends along the *bc* plane (Fig. 2). In the sheet, the Cu^{2+} ions are not all in the same plane. As the neighbouring $[\text{Cu}(\text{phen})(\text{dca})_2]_n$ chains in the sheet are centrally symmetric, the phen ligands are arranged on both sides of the sheet, and the planes of the phen ligands are inclined with respect to the *bc* plane at an angle of *ca* 70°. Finally, these sheets stack along the *a* direction through aromatic interactions between interlocking phen ligands from adjacent sheets, to build the three-dimensional crystal structure.

(Potočňák *et al.*, 1995, 1996; Dunaj-Jurčo *et al.*, 1996; Kurmo & Kepert, 1998; van Albada *et al.*, 2000). Among them, only one of these co-ligand complexes is a polymeric compound

In the CuN_5 pyramid, the four basal Cu–N distances, being in the range 1.959 (3)–2.024 (2) Å, are nearly equal to each other, and are similar to those of the pyramidal CuN_5 moiety in $[\text{Cu}(\text{add})(\text{bipy})(\text{dca})]$ (add is 3-amino-3-methoxy-2-nitrosoacrylonitrilate and bipy is 2,2'-bipyridine; Dunaj-Jurčo *et al.*, 1996) or to the equatorial Cu–N distances of the tetragonal bipyramidal CuN_6 moiety in $[\text{Cu}(\text{phen})_2(\text{dca})_2]$ (Potočňák *et al.*, 1995), $\text{Cu}(\text{dca})_2$ (Kurmo & Kepert, 1998) and $[\text{Cu}(\text{dca})_2(\text{ampym})_2]$ (ampym is 2-aminopyrimidine; van Albada *et al.*, 2000). The axial Cu–N distance [2.286 (3) Å] is slightly longer than in the pyramidal CuN_5 moiety reported by Dunaj-Jurčo *et al.* (1996) [2.188 (4) Å]. The secondary or weak Cu–N bond aforementioned, which has a Cu–N distance of 2.821 (3) Å and is opposite to the axial Cu–N bond, is unusually longer than long Cu–N bonds reported previously for Cu–dca complexes [2.449 (4) and 2.473 (4) Å in $\text{Cu}(\text{dca})_2$ (Kurmo *et al.*, 1998), and 2.365 (3) Å in $\text{Cu}(\text{phen})_2(\text{dca})_2$ (Potočňák *et al.*, 1995)]. If this secondary Cu–N bond is included, the Cu^{2+} ion has a 5 + 1 coordination environment.

The intrachain Cu–Cu distance of 7.7079 (4) Å is longer than the shortest interchain Cu–Cu distance of 6.4521 (4) Å between two Cu^{2+} ions related by the screw axis 2_1 (010) and with no spacer between them. Another short interchain Cu–Cu distance of 7.3002 (7) Å is between the two Cu^{2+} ions connected by two dca ligands *via* the secondary Cu–N bonds.

The bond distances and angles in the phen ligand, which range from 1.318 (4) to 1.431 (5) Å and 116.2 (3) to 125.5 (3)°,

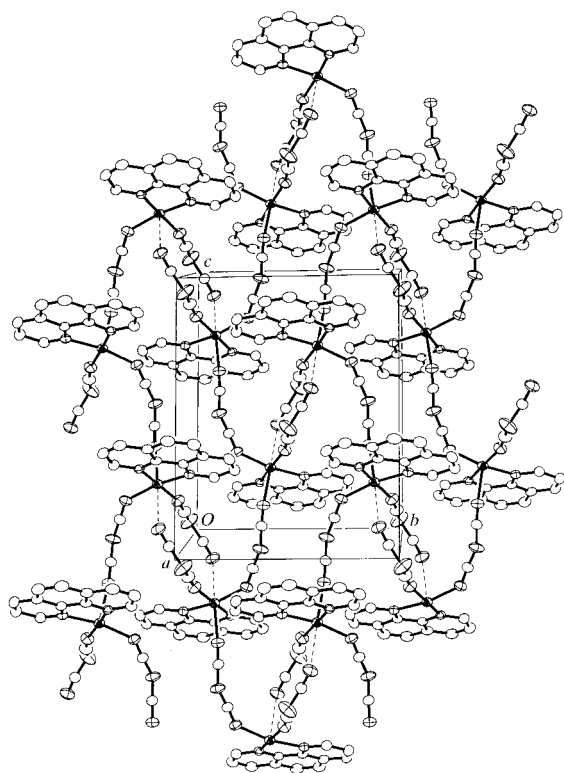


Figure 2
The sheet structure of (I) showing 30% probability displacement ellipsoids. The dashed lines show the secondary Cu–N bonds. H atoms have been omitted for clarity.

respectively, are all normal (Potočňák *et al.*, 1995). The phen ligand is nearly planar, with the largest deviation from the mean plane being 0.064 (3) Å for C2. The dca ligands are also planar and the largest deviation from the mean plane is 0.019 (3) Å for C14. Two distinct sets of N–C distances in the dca ligands, which lie in the ranges 1.098 (4)–1.149 (4) Å and 1.283 (4)–1.331 (5) Å, together with the C–N–C [120.5 (4) and 122.3 (3)°] and N–C–N angles [167.1 (4)–174.2 (3)°], are all comparable with values found in other dca complexes (Kurmo & Kepert, 1998; Batten *et al.*, 1999; Manson, Arif, Incarvito *et al.*, 1999; Potočňák *et al.*, 1995, 1996; Dunaj-Jurčo *et al.*, 1996; van Albada *et al.*, 2000).

We have also obtained the Co analogue (Sun *et al.*, 2000) of this structure. The main difference between the two structures is that in the Co complex, the Co atom is sixfold coordinated in an octahedral coordination environment in which no weak secondary Co–N bonds exist and the Co–N distances fall in the range 2.081 (3)–2.207 (2) Å. A similar behaviour has been observed for the two related structures $\text{Cu}(\text{dca})_2$ and $\text{Co}(\text{dca})_2$. This pattern is related to the strong Jahn–Teller effect which influences the Cu^{2+} ion (Kurmo & Kepert, 1998).

Experimental

A 4 ml ethanol solution containing hydrated phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, 59.5 mg, 0.30 mmol) and a 4 ml ethanol solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (59.9 mg, 0.30 mmol) were mixed and stirred for 5 min. A 2 ml aqueous solution of $\text{NaN}(\text{CN})_2$ (26.7 mg, 0.30 mmol) was then added to the above solution and the resulting solution stirred for another 5 min. The clear blue solution was filtered. Blue block-shaped crystals were obtained after slow evaporation of the filtrate over a period of one week (yield 22%). Analysis calculated for $\text{C}_{16}\text{H}_8\text{CuN}_8$: C 51.13, H 2.15, N 29.82, Cu 16.91%; found: C 51.39, H 2.24, N 29.81, Cu 19.5% (by inductively coupled plasma).

Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)]$	$D_x = 1.607 \text{ Mg m}^{-3}$
$M_r = 375.84$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 27 425 reflections
$a = 9.8389$ (3) Å	$\theta = 3.43$ – 27.84°
$b = 11.2975$ (5) Å	$\mu = 1.423 \text{ mm}^{-1}$
$c = 14.2340$ (5) Å	$T = 293$ (2) K
$\beta = 100.988$ (2)°	Block, blue
$V = 1553.17$ (10) Å ³	$0.25 \times 0.22 \times 0.13 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (Å, °).

Cu1–N3	1.959 (3)	Cu1–N2	2.024 (2)
Cu1–N6	2.003 (3)	Cu1–N8 ⁱ	2.286 (3)
Cu1–N1	2.010 (2)	Cu1–N5 ⁱⁱ	2.821 (3)
N3–Cu1–N6	90.97 (13)	N1–Cu1–N8 ⁱ	91.35 (10)
N3–Cu1–N1	172.10 (11)	N2–Cu1–N8 ⁱ	96.74 (10)
N6–Cu1–N1	93.18 (11)	N1–Cu1–N5 ⁱⁱ	81.81 (9)
N3–Cu1–N2	92.58 (11)	N2–Cu1–N5 ⁱⁱ	81.79 (10)
N6–Cu1–N2	164.49 (10)	N3–Cu1–N5 ⁱⁱ	92.04 (11)
N1–Cu1–N2	81.68 (9)	N6–Cu1–N5 ⁱⁱ	83.00 (11)
N3–Cu1–N8 ⁱ	94.72 (12)	N8 ⁱ –Cu1–N5 ⁱⁱ	173.14 (10)
N6–Cu1–N8 ⁱ	98.01 (11)		

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

Data collection

Nonius KappaCCD diffractometer
 CCD scans
 Absorption correction: empirical
 (Blessing, 1995, 1997)
 $T_{\min} = 0.766$, $T_{\max} = 0.831$
 27 425 measured reflections
 3682 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.120$
 $S = 1.015$
 3682 reflections
 227 parameters
 H-atom parameters constrained

2489 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$
 $\theta_{\text{max}} = 27.84^\circ$
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = -18 \rightarrow 18$

$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.6068P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0046 (10)

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *HKL Scalepack* (Otwinowski & Minor, 1997); data reduction: *HKL Denzo* (Otwinowski & Minor, 1997) and *maXus* (Mackay *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1104). Services for accessing these data are described at the back of the journal.

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