

catena-Poly[[dicyanamido(5,5'-dimethyl-2,2'-bipyridine- κ^2 N,N')-copper(II)]- μ -dicyanamido- κ^2 N¹:N⁵]

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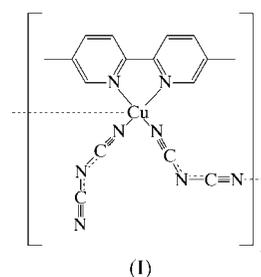
In the crystal structure of the title compound, $[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)]_n$, the Cu^{II} atom adopts a distorted square-pyramidal geometry, the basal plane of which is formed by two N atoms of the bipyridine ligand, one N atom of a bidentate dicyanamido anion and one N atom of a monodentate dicyanamido anion [$\text{Cu}-\text{N} = 1.9760(15)-2.0157(15) \text{ \AA}$]. The apical position is occupied by an N atom of a bidentate dicyanamido anion, located $2.2468(16) \text{ \AA}$ from the Cu atom, thus forming a one-dimensional polymeric chain.

Comment

Dicyanamide complexes have attracted much interest in recent years as a new class of magnetic materials, especially in the form of $M^{\text{II}}[\text{N}(\text{CN})_2]_2$ (M is Ni, Co, Cu or Zn) (Batten *et al.*, 1998; Jensen, Batten, Fallon, Moubaraki *et al.*, 1999; Jensen *et al.*, 2001; Kohout *et al.*, 2000; Manson *et al.*, 1998, 1999; Miller & Manson, 2001). The X-ray structures of a number of compounds containing the dicyanamide anion and copper(II) have been reported (Potočňák *et al.*, 2001; Riggio *et al.*, 2001; Martín *et al.*, 2001). Dicyanamide itself is a most interesting anionic bridging ligand. It can act as a monodentate, bidentate (with two distinct types of binding) or even tridentate ligand (Mroziński *et al.*, 1997; Escuer *et al.*, 2000). However, X-ray structures of polymeric compounds with Cu^{II} and dicyanamide with the general formula $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(L)_y]_n$ ($y = 1$ or 2 and L is a coordinating organic molecule) are very rare. Currently, only six crystal structures of this type of compound have been reported in which four different types of polymeric network can be discerned.

A one-dimensional network (type A, Fig. 2) is found in $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(2\text{-aminopyrimidine})_2]_n$ (van Albada *et al.*, 2000). Dicyanamide and Cu^{II} cations form an infinite chain, with two dicyanamide anions bridging between each pair of

Cu^{II} cations. β - $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{pyrazine})_2]_n$ (Jensen, Batten, Fallon, Hockless *et al.*, 1999) forms a two-dimensional network (type B, Fig. 2), in which one of the base directions is the structural element found in the previous compound, and the second base direction is formed by the pyrazine ligand, which forms a bridge between two adjacent $\text{Cu}[\text{N}(\text{CN})_2]_2$ chains. The compounds α - $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{pyrazine})_2]_n$ (Jensen, Batten, Fallon, Hockless *et al.*, 1999), $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{pyrimidine})_2]_n$ (Riggio *et al.*, 2001) and $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{bipyrimidine})]_n$ (Martín *et al.*, 2001) form three-dimensional networks (type C, Fig. 2). This type of network consists of two-dimensional $\text{Cu}[\text{N}(\text{CN})_2]_2$ sheets, with a single dicyanamide anion between each pair of Cu^{II} cations. The third dimension is obtained by linking these copper–dicyanamide sheets through the organic ligand, in a similar way to that found in the two-dimensional networks of type B. The fourth network type (type D, Fig. 2) is found for the compounds $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(1,10\text{-phenanthroline})_2]_n$ (Wang *et al.*, 2000) and $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(3\text{-hydroxypyridine})_2]_n$ (van Albada *et al.*, 2001). These compounds form an infinite one-dimensional chain, with only one dicyanamide anion bridging between each pair of Cu^{II} cations. The second dicyanamide is monodentate and the organic ligand coordinates only to a single Cu^{II} cation. The title compound, (I), is a new example of a type D network.



The geometry around the Cu^{II} ion in (I) is distorted square pyramidal. The basal plane is formed by the two N atoms of the 5,5'-dimethyl-2,2'-bipyridine ligand (N11 and N21), one N atom of the monodentate dicyanamido anion (N3) and one terminal N atom of the bridging dicyanamido anion (N6). The $\text{Cu}-\text{N}$ distances vary from $1.9760(15)$ to $2.0157(15) \text{ \AA}$. The apical position is occupied by the other terminal N atom of the bridging dicyanamido anion (N5) at a distance of $2.2468(16) \text{ \AA}$ from the Cu^{II} ion. The distortion of the square pyramid can be described by the parameter τ (τ describes the relative amount of trigonality; $\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid; Addison *et al.*, 1984). For complex (I), the value of τ is 0.21.

The $\text{Cu}\cdots\text{Cu}$ distance along the polymeric chain of (I) is $7.5297(10) \text{ \AA}$, *i.e.* equal to the length of the a axis. The Cu –dicyanamide– Cu distances reported for the complexes discussed above all lie in the range 7.39 – 7.71 \AA , with the exception of the distances observed in the α form of the pyrazine complex (Jensen, Batten, Fallon, Hockless *et al.*, 1999), belonging to network type C, which are in the range 8.64 – 8.83 \AA . On the basis of the Cu –dicyanamide– Cu distances, no clear distinction can be made between Cu complexes of different network types.

In the complexes with network type *D*, $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2\text{-}(3\text{-hydroxypyridine})_2]_n$ (van Albada *et al.*, 2001) and $[\text{Cu}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(1,10\text{-phenanthroline})_2]_n$ (Wang *et al.*, 2000), there is a close contact between the Cu^{II} ions and the remaining terminal N atoms of the monodentate dicyanamide anions. These N atoms occupy the second apical site of the Cu^{II} ions, at distances from the Cu^{II} of 2.97 and 2.82 Å for the hydroxypyridine and phenanthroline complexes, respectively. In (I), the second apical site of the Cu^{II} ion is occupied by the remaining terminal N atom (N2), located at a distance of 3.006 (2) Å from Cu1. Although rather long for an interaction, this distance is still 0.86 Å shorter than the sum of the van der Waals radii. The relatively high displacement parameters of N2 indicate that it has only a weak interaction with Cu1.

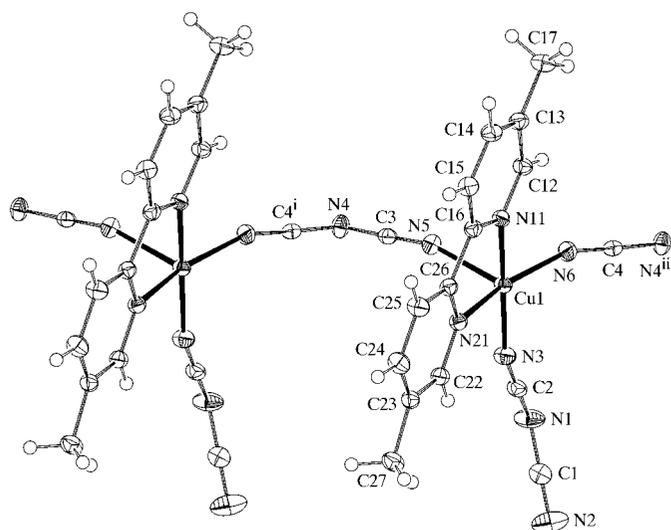


Figure 1
A view of the structure of (I) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level [symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$].

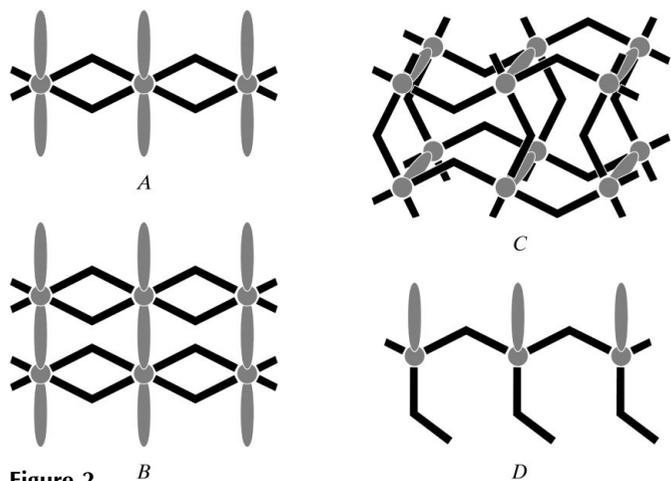


Figure 2
The network types found for $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(L)_y]_n$, where *L* is a coordinating organic ligand with either one (type *A* or *D*) or two (type *B*, *C* or *D*) coordinating atoms. Cu^{II} ions are shown as grey spheres, organic ligands (*L*) as grey ellipsoids and $\text{N}(\text{CN})_2$ anions as thick black lines.

If these additional contacts are considered as true interactions, the description of the polymeric structures of type *D* complexes has to be expanded. In the hydroxypyridine complex, the dicyanamide anions have orientations similar to those found in networks of type *A* (the aminopyridine complex), meaning that N2 is in close contact with the neighbouring Cu^{II} ion within the infinite one-dimensional network. In (I), atom N2 has a close contact with a Cu^{II} ion of a neighbouring $\text{Cu}\{\text{N}(\text{CN})_2\}_2$ chain, resulting in a two-dimensional network of Cu^{II} cations and dicyanamide anions (Fig. 3), similar to the sheets found in networks of type *C*. In contrast with those networks, however, the dimethylbipyridine ligand in (I) interacts with only one Cu^{II} ion, so the two-dimensional networks are not linked to each other and a three-dimensional network is not formed. In the phenanthroline complex, a two-dimensional network is found, related to that present in (I). In this network, however, not all dicyanamide links between Cu^{II} ion pairs are present, while others are doubled, *i.e.* are formed by two bridging anions.

The crystal lattice of (I) is further stabilized by weak $\pi \cdots \pi$ interactions. The pyridine ring containing N21 is stacked on the inversion images generated by the symmetry operation $(2 - x, -y, -z)$. The distance between the geometric centres of the rings is 3.6749 (11) Å.

The ligand field spectrum of the Cu^{II} derivative shows a broad *d-d* transition band centred around $14.5 \times 10^3 \text{ cm}^{-1}$, with a shoulder at the low-energy side. The characteristic IR vibrations for the dicyanamide anion are the $\nu_s + \nu_{\text{as}(\text{CN})}$ vibrations. These vibrations are found as a strong band at 2289 cm^{-1} , two medium strong bands at 2248 and 2229 cm^{-1} , and a broad very strong band at 2160 cm^{-1} , with a shoulder at 2175 cm^{-1} . The electron paramagnetic resonance (EPR) spectrum, measured on (I) as a polycrystalline powder, shows an axial $S = \frac{1}{2}$ spectrum with $g_{\perp} = 2.09$ and g_{\parallel} (very weak broad) = 2.26, values typical for Cu^{II} . These values are in agreement with observations made earlier by Riggio *et al.* (2001).

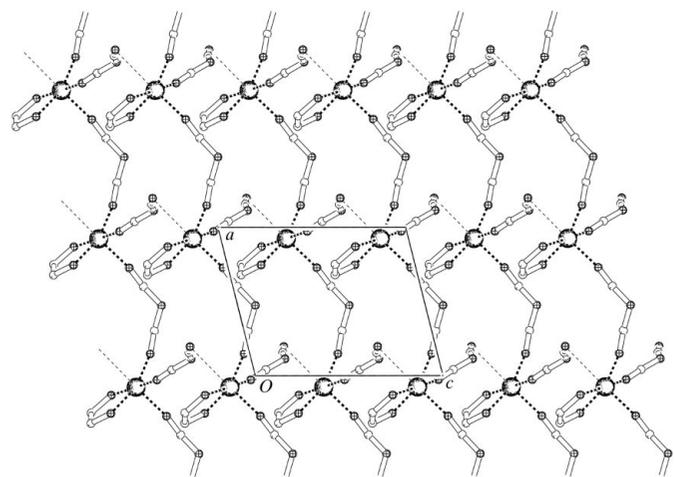


Figure 3
Part of the infinite two-dimensional network formed in (I) by $\text{Cu}-\text{N}$ bonds and contacts, projected along the *b* axis. The long $\text{Cu} \cdots \text{N}$ contact (3.00 Å) is indicated by a thin dashed line. For clarity, only the $\text{N}-\text{C}-\text{C}-\text{N}$ fragment of the dimethylbipyridine ligand is shown.

The magnetic susceptibility of powdered samples of (I) was measured from 5 to 300 K. The plot of μ_{eff} versus temperature gives hardly any changes at lower temperatures and stays constant at a value of 1.70–1.85 BM down to 5 K, which is close to the spin-only value for Cu^{II} . Given the fact that the magnetic ($d_{x^2-y^2}$) orbitals of neighbouring Cu^{II} ions are mutually orthogonal (the four short Cu–N bonds are within the same planes) and the other Cu···Cu distances are large (5.96 Å), one would not expect any significant interactions. So, in the present case, at best a very weak antiferromagnetism is present ($J > -1 \text{ cm}^{-1}$), as down to 5 K no maximum in χ is observed.

Experimental

Physical measurements and the synthesis of (I) were performed according to the methods described by Riggio *et al.* (2001). Yield 65%; elemental analysis, found: C 50.3, H 3.1, N 29.3%; $\text{C}_{16}\text{H}_{12}\text{CuN}_8$ requires: C 50.6, H 3.2, N 29.5%.

Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)]$	$D_x = 1.574 \text{ Mg m}^{-3}$
$M_r = 379.89$	MoK α radiation
Monoclinic, $P2_1/c$	Cell parameters from 569 reflections
$a = 7.5297 (10) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 23.628 (3) \text{ \AA}$	$\mu = 1.38 \text{ mm}^{-1}$
$c = 9.2916 (10) \text{ \AA}$	$T = 150 \text{ K}$
$\beta = 104.175 (10)^\circ$	Block, blue
$V = 1602.8 (3) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 29 951 measured reflections
 3647 independent reflections
 3199 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -9 \rightarrow 9$
 $k = -30 \rightarrow 30$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R(F) = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.06$
 3647 reflections
 228 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 1.15P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1–N3	1.9760 (15)	Cu1–N11	2.0157 (15)
Cu1–N5	2.2468 (16)	Cu1–N21	2.0045 (14)
Cu1–N6	1.9841 (16)		
N3–Cu1–N5	94.41 (6)	N5–Cu1–N11	100.40 (6)
N3–Cu1–N6	91.20 (6)	N5–Cu1–N21	89.92 (6)
N3–Cu1–N11	93.76 (6)	N6–Cu1–N11	161.18 (6)
N3–Cu1–N21	173.50 (6)	N6–Cu1–N21	93.05 (6)
N5–Cu1–N6	97.30 (6)	N11–Cu1–N21	80.68 (6)

H atoms were placed at calculated positions, riding on their carrier atoms. The methyl H atoms were refined as rigid groups, allowing for rotation around the C–C bond. Isotropic displacement parameters for H atoms were coupled to the equivalent isotropic displacement parameter of the carrier atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1091). Services for accessing these data are described at the back of the journal.

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